

# HANDBOOK OF ADHESIVES

**Edited by Irving Skeist**





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## Third Edition

Edited by

**Irving Skeist, Ph.D.**

*Consultant to the Polymer Industries  
Skeist Incorporated  
Whippany, New Jersey*



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# Preface

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Adhesives are indispensable. They are required in myriad products—aircraft and abrasives, cars and cartons, shoes and safety glass, tape and tires. This Third Edition of *Handbook of Adhesives*, like the 1962 and 1977 editions, seeks to provide the knowledge needed for optimum selection, preparation, and utilization of adhesives and sealants. The information is detailed and explicit, with several hundred illustrative formulations.

Expert information has been supplied in 47 chapters written by 70 industry specialists, professors, and consultants. Five chapters on fundamentals provide the theoretical and economic underpinnings—why adhesives work, how they are selected, how the surface is prepared, how they are applied, how they are set, how the cured joint is tested. The economic importance of the adhesive-using industries is spelled out, with specifics on the role of adhesives in construction, packaging, autos, aircraft/aerospace, textiles, footwear, abrasives, electronics, and in the home. The next 28 chapters cover the adhesive materials—thermosetting, thermoplastic, elastomeric, natural polymers, cou-

pling agents, and other key ingredients. Special attention is given to such flourishing categories as acrylics, anaerobics, cyanoacrylates, polyurethanes, epoxy resins, polyvinyl acetate, high temperature adhesives, hot melts, silicones, and silanes.

The last 14 chapters, on adherends and bonding technology, involve the auto industry, aircraft, electronics, the bonding of wood, textiles, rubber and plastics, construction, abrasives, pressure-sensitives, nonwovens, and sealants. Mechanical handling of two-component systems is examined. The concluding chapter highlights the exciting progress that is being made in the use of robotics to apply adhesives, techniques already far advanced in automotive assembly.

To Jerry Miron and Arnold Brief of Skeist Incorporated, my long time consulting associates, I express my gratitude and appreciation for their invaluable support.

IRVING SKEIST  
*Whippany, New Jersey*



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# HANDBOOK OF ADHESIVES

# Section A

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## Fundamentals

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# Introduction to Adhesives

IRVING SKEIST AND JERRY MIRON

*Skeist Incorporated  
Consultants to the Polymer Industries  
Whippany, New Jersey*

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Adhesives are social substances. They unite materials, creating a whole that is greater than the sum of its parts. They are small in volume compared to the metals, glass, wood, paper, fibers, rubber, and plastics that they join together; but just as enzymes, hormones, and vitamins are required for individual well-being, the adhesives are recognized as essential to the health of our industrial society.

## **ADVANTAGES OF ADHESIVE BONDING**

The rapid growth of the adhesives industry has resulted from its many advantages over other methods of joining materials:

1. Thin films, fibers and small particles, that could not be combined as well, or at all, by other techniques, are readily bonded with adhesives. Typical of such uses are:

- (a) Laminates of plastic films, aluminum foil, fabrics, and paper.
- (b) Glass wool insulation and fiber glass mat composites.
- (c) Abrasive wheels, sandpaper, emery cloth, and brake linings.
- (d) Tires reinforced with rayon, nylon, polyester, glass fiber, and steel.

- (e) Corrugated board, paper bags, labels, tapes, stamps, and envelopes.
- (f) Safety glass.
- (g) Nonwoven fabrics, flocked fabrics, and tufted carpets.
- (h) Clay-coated paper for printing.
- (i) Particle board.
- (j) Veneer furniture.

2. Stresses are distributed over wider areas, making possible lighter and stronger assemblies than could be achieved with mechanical fastening. For example, airplane wings, tails, and fuselages may be constructed of sandwich panels comprising a honeycomb core bonded to thin faces of aluminum or magnesium; consequently the possibility of fatigue failure is decreased. Glued floors, wood framing and entire room modules, factory-prebuilt for economy, have the tensile, flexural, and impact strength to resist the rigors of transportation and hoisting into place. In reinforced plastics and advanced composites, glass fiber is adhered to the unsaturated polyester matrix, or graphite fiber to epoxy matrix, with the aid of functional silanes and other coupling agents.

3. The strength-to-weight ratios and dimensional stability of anisotropic materials can be improved by cross-bonding. Thus wood, inherently nonuniform and water-sensitive, is

converted into warp-resistant, water-resistant plywoods. Nonwoven fabric having the same properties in all directions is made by lightly bonding a random web of fiber.

4. The glue line provides electrical insulation in capacitors, printed circuits, motors, potted resistors, etc.

5. The glue line can be a moisture barrier, sealing window panels in curtain wall construction. In laminates for packaging, the glue line adds greatly to the moisture-vapor resistance.

6. Dissimilar materials can be joined, e.g., aluminum-to-paper, iron-to-copper. When two metals are bonded, the adhesive separates them and prevents corrosion. When the two adherends are markedly different in coefficient of thermal expansion, a flexible adhesive lessens the stress due to temperature change. Laminates of dissimilar materials can give combinations superior to either adhered alone; for example, a polyethylene-cellophane composite has the heat-sealability and water-resistance of the former plus the grease-resistance and printability of the latter.

7. Finally, what is often the key consideration: adhesive bonding may be faster and cheaper than the weaving of cloth; soldering, brazing or welding of metals; or mechanical fastening of rivets, bolts, or nails.

## HISTORY

Adhesives were utilized in a sophisticated manner even in ancient times. Carvings in Thebes dating back 3300 years depict the gluing of a thin piece of veneer to what appears to be a plank of sycamore. The glue pot and brush are shown.<sup>1</sup> Still earlier, in the palace of Knossos in Crete, wet lime was the binder for chalk, iron ocher, and copper blue frit pigments with which the walls were painted.<sup>2</sup> The Egyptians utilized gum Arabic from the acacia tree, egg, glue, semiliquid balsams, and resins from trees. Wooden coffins were decorated with pigments bonded with "gesso," a mixture of chalk and glue.

Papyrus was an early nonwoven fabric. Reeds 12 to 20 ft high and 3 in. in diameter were cut in thin slices, laid side by side, and beaten with a mallet. After these were brushed over with flour paste, fresh slices of reed were

laid at right angles, and the beating was repeated. The finished papyrus was a luminous brown.<sup>2</sup>

We read in Genesis that slime (bitumen) was the preferred mortar of the builders of the Tower of Babel—the first adhesives technologists to have problems of semantics. Bitumen and tree pitches were the sealants for the vessels that plied the Mediterranean. In the days of the prophets, as now, the adhesive had to be specific for the adherend. "He that teacheth a fool is like one that glueth potsherds together," we are advised in the Apocrypha (Jesus ben Sirach, Ecclesiasticus, Chapter 22). Educators are still struggling with the first problem, but the latter has been solved with epoxy adhesives.

According to Pliny, the Romans caulked their ships with pine wood tar and beeswax. Anticipating the laminate and the printed circuit, Pliny described the application of gold leaf to paper with egg white. We learn also that the Romans, like the ancient Chinese, made bird lime, an adhesive from the juice of the mistletoe, with which they smeared twigs to catch small birds.

Glues from fish, stag horns, and cheese were known in the days of Theophilus for fixing together wooden objects. Here is his ninth century recipe for *glutine casei*:

"Soft cheese is cut very small, and is washed with warm water in a small mortar with a pestle, until, being frequently poured in, the water comes away pure. Then this cheese, compressed by the hand, is put into cold water until it hardens. After this it is very finely ground, with another piece of wood, upon a smooth wooden table, and in this state it is again placed in the mortar, and is carefully ground with the pestle, water mixed with quick lime being added, until it is made as thick as lees. The tablets of altars fastened together with this glue, after they are dry, so adhere together, that neither heat nor humidity are able to disjoin them."

Except for the introduction of rubber and pyroxylin cements a hundred years ago, there was little advance in adhesives technology until well into the twentieth century. In these last few decades, the natural adhesives have been im-

proved, and a spate of synthetics has poured from the laboratories.

## INFORMATION SOURCES

The second edition (1977) showed some 40 books on adhesives and adhesion since 1947. Another score of more recent volumes are listed in the References to this chapter,<sup>3-21</sup> along with eight periodicals from six countries,<sup>22-29</sup> of which *Adhesives Age*<sup>24</sup> is the most widely known.

The Gordon Research Conferences, the American Chemical Society, and many universities are among the organizations which sponsor symposia on adhesion and adhesives.

Techno-economic studies of the adhesives industry are prepared by various consulting firms, including ours.

## TYPES OF ADHESIVES

Adhesives may be classified in many ways, e.g., by mode of application and setting, chemical composition, cost, and suitability for various adherends and end products.

### Application and Setting

The adhesive must be applied to the substrate in a fluid form to wet the surface completely and leave no voids, even if the surface is rough. Consequently, the adhesive must be low in viscosity at the time of application.

To develop high cohesive strength, however, the adhesive must set. In a completed joint with an organic adhesive, the latter layer is either a *soluble*, usually *thermoplastic* and *fusible* material of extremely high viscosity, or a *cross-linked*, *infusible* thermoset resin or rubber.

The transition from fluid to solid may be accomplished in several ways:

1. *Cooling of a Thermoplastic.* Thermoplastics soften and melt when heated, becoming hard again when cooled. The heating must result in sufficiently high fluidity to achieve successful wetting. The thermoplastic may be coated on one substrate by various techniques:

- from hot-melt,
- as a powder,
- by extruder,

- from solvent or latex followed by drying and cooling.

By convention, "hot-melt" often denotes a lower molecular weight, less viscous material than "thermoplastic."

If the cooled coating is not tacky, the coated substrates can be piled and stored for future use, when they will have to be heated to reactivate the adhesive. Alternatively, the bond is often made immediately after application of the hot-melt, powder, or extruded coating. This procedure offers best production rates, since the cooling of a hot-melt is faster than evaporation of solvent or chemical setting.

Paper, paperboard, and cellophane for food packaging present examples of the various modes of applying thermoplastic adhesives. The substrate can be protected with a heat-sealable moisture barrier by kiss-coating the web with molten wax, for bread wraps; by extruder-coating with polyethylene, for milk cartons and multiwall bags; or by applying a saran solution or latex and evaporating the solvent or water. Where resistance to moisture is not needed, as in the sealing of cartons containing cans, a reduction in cost is achieved by applying the heat-sealable adhesive as a powder rather than a continuous film. Acrylic and vinyl copolymer powdered resins have speeded production of some types of nonwovens.

Two important determinants of strength in hot-melts are molecular weight and polarity. Thus paraffin wax and polyethylene are both aliphatic hydrocarbon polymers; but the far greater molecular weight of the polyethylene results in much higher tensile strength, tear strength, and heat resistance.

Several families of hot-melts now offer still greater strength. The EVA's are ethylene-vinyl acetate copolymers which are compounded with waxes and tackifiers to make adhesives for packaging, bookbinding, and furniture edge-banding. Polyamides and polyesters are employed for the soling of shoes, the edge-banding of furniture, and the side-seaming of cans.

While the rapid setting of hot-melts is usually desirable, there is at least one exception. Labels for bottles and cans are sometimes coated with a "delayed tack" adhesive, e.g., polyvinyl acetate formulated with a plasticizer



that is solid at room temperature, so that when activated by heat, the label remains sticky for as long as a minute, facilitating the operation of a high-speed packaging line.

Safety glass for automobiles is a sandwich of highly plasticized polyvinyl butyral, a thermoplastic, between two sheets of plate glass. The compounded PVB must be optically clear, stable to light, and free from volatiles; but above all, it must be tough and a good adhesive, holding glass fragments tenaciously in case of accident which cracks the glass.

Perhaps the largest volume hot-melt of all is the asphalt which binds aggregate on our road surfaces.

2. *Release of Solvent or Carrier.* Solutions and latexes contain the adhesive composition in admixture with water or organic solvents. These liquids lower the viscosity sufficiently to permit wetting of the substrate. Once this has been accomplished, however, they must be removed. Porous substrates such as paper permit the liquid to be drawn away from the glue layer. If both adherends are impermeable, however, it is necessary to evaporate the water or solvent before mating the two surfaces, thus slowing down production. This is the great disadvantage of solutions and latexes in adhesive applications. In addition, organic solvents may be undesirable because of cost, shortages, flammability, toxicity, or tendency to pollute. In recent years, regulations such as Los Angeles County's Rule 66 have established upper limits on the amounts of various solvents that are permitted as effluents from industrial applications.

Thus the three E's—Economy, Energy, and Environment—are in opposition to solvent-based adhesives. Nevertheless, their excellent wetting characteristics, plus applicability at low temperatures and high coverage, will enable them to retain an important role.

In a *solution*, the concentration of "solids"—i.e., material which will remain in the final adhesive layer—is usually under 30% for organic solvents but may be higher with water as the solvent, and especially in latexes. For a solution, too great a solids content results in such high viscosity that the dope has poor wetting characteristics. The higher the molecular weight of the dissolved polymer, the lower is the maximum permissible concentration.

Therefore, in the manufacture of solvent cements, one employs resins having far lower molecular weights than those preferred for plastics and elastomers. The "half second" cellulose esters and nitrocellulose are examples of short-chain polymers which are adequate as adhesives, but might be too weak as plastics.

*Water* is not only the carrier for latexes but is also the most important of the solvents. Starches and dextrans, protein glues, and polyvinyl alcohol are the more significant water-soluble organic adhesives. Sodium silicates, comprising the most important family of inorganic adhesives, are water soluble.

To achieve concentrations above 50% it is necessary that at least a portion of the polymer be present in agglomerates of greater than colloidal size. In a *latex*, the polymer is present in the form of globules existing as a discrete phase in an aqueous matrix. Natural and synthetic rubbers, vinyl resins, and acrylics are the most important of the adhesive latexes. The polymer is not limited in molecular weight since the viscosity does not depend on what is contained within the discrete particles. The viscosity of the latex depends primarily on solids content and the composition of the aqueous phase. Latexes are commonly available in concentrations of 35 to 55%; but it is possible, in some cases, to go considerably higher before reaching an excessive consistency.

In many operations, for example the coating of paper on the machine at high speeds, the elimination of water becomes a bottleneck. In choosing a binder for clay and pigment, there is an increasing tendency to abandon starch solutions in favor of combinations of casein or soy protein with synthetic latexes.

*Organosols* are akin to latexes in being two-phase compositions, but with a continuous organic phase instead of water. Organosols are dispersions of vinyl chloride resin in plasticizers and volatile organic solvents. Once again, they are sufficiently fluid to promote good wetting of the substrate, which may be paper, cloth, or metal. After application to the substrate, the coating is heated to flash off the solvent and fuse the resin.

3. *Polymerization in situ.* This is the group of bonding agents making the most rapid technological progress. All the thermosetting resins

come under this heading, including those which are first applied to the substrate in solution form. This category also includes elastomers that are vulcanized to develop higher cohesive strength. In addition, some vinyl-type monomers, especially methyl methacrylate, cyanoacrylate esters, and the dimethacrylates, are polymerized readily *in situ*.

The main advantage of these materials over solvent-based adhesives is that strength can be developed in the glue line after the two adherends have been brought together. Faster production, lower cost, and stronger bonds may result from the elimination of solvents.

The reaction-sensitive adhesives fall into two groups:

1. Those formed by *condensation*, usually with water as a by-product. This group includes the phenolic and amino resins, which are the oldest of the all-synthetic adhesives.
2. Those formed by *addition polymerization* without by-product formation. Among this group are several of the most interesting of the new adhesives, including polyesters, epoxies, urethanes, cyanoacrylates, anaerobics, and radiation-curable polymers. Conventional acrylics and vulcanizing rubbers are also in this category.

When a composite is made with an adhesive from group (1), it is necessary to apply pressure to overcome the deleterious influence of the water or other volatile by-product. On the other hand, adhesives of group (2) may be cured with only contact pressure. This is especially advantageous in the preparation of large objects which cannot be conveniently placed in a press.

Some of the curing adhesives require heat, whereas others react at room temperature with the help of catalysts, and in some instances with activation by light. Again, it is an advantage to make a bond without the aid of an oven. Among the adhesives which can be processed in the cold, with proper formulation, are resorcinol formaldehyde, unsaturated polyesters, methyl methacrylate, cyanoacrylate esters, epoxies, and urethanes. The polymerization reaction is usually exothermic, so that the glue line may become somewhat warmer than the ambient

temperature, especially if the adherends are poor conductors of heat.

For some decades, dentists have filled cavities with pastes of polymethyl methacrylate in monomeric MMA. Now, adhesives companies are offering similar formulations for industrial applications.

The *anaerobic* adhesives, a development of recent years, are dimethacrylates which, when properly compounded, remain liquid so long as oxygen is present, but cure rapidly when air is excluded. They have rapidly achieved wide usage in metal assembly. They are covered in a separate chapter in this volume.

The term *aerobic* adhesives is being advanced for a series of two-component structural acrylic adhesives which have reduced sensitivity to oxygen inhibition. In contrast to the anaerobic adhesives, they can be applied to porous surfaces and to fill wider gaps, e.g., up to 60 mils.<sup>60</sup>

The *radiation-curable* adhesives are most commonly either polymers with acrylate side chains or unsaturated polyesters. They can be cured by ultraviolet light or by electron beam radiation, which has greater penetration but is more costly. Acrylate-type U.V.-curable coatings have achieved an important place in the coil-coating of steel and aluminum. For adhesives, the technique is less useful; but it has been employed for the sealing of electric light bulbs. Also, an ingenious method for making nonwoven webs involves the cryogenic polymerization of frozen monomer with the aid of U.V. radiation.

4. *Pressure-Sensitive Adhesives*.<sup>16</sup> These adhesives, unlike the other classes, do not undergo a progressive increase in viscosity. Instead, they are permanently in the intermediate *tacky* stage. One of their chief merits for some applications, in fact, is that they wet so inadequately that they can be removed from the adherend surface without "mark off," i.e., without leaving a residue of adhesive on that surface. One of the important early advances in pressure-sensitive tape technology was the discovery that a slightly gelled adhesive layer would fulfill this requirement.

While this deficiency in adhesive strength is deliberate, the low cohesive strength of pressure-sensitive materials is undesirable. Low

bond strength precludes the pressure-sensitive tapes from heavy-duty applications. It is inevitable that a permanently tacky material will be easily deformed and ruptured.

Most pressure-sensitive masscoats contain a blend of elastomers—natural rubber, reclaim and SBR—with tackifiers of low or medium molecular weight, antioxidants, etc. These are applied to the web-tape or label backing from solutions; but the newer “thermoplastic elastomers”—block copolymers of styrene with isoprene or butadiene—can be applied from melt. Where excellent color and resistance to light and oxidation are needed, the higher priced acrylic ester copolymers are preferred. Polyisobutylene, also resistant to ultraviolet degradation, is utilized for removable labels.

Two sided pressure-sensitive tapes, as well as most PS labels, are interlined with release paper to prevent them from sticking together prior to use. The *adhesive* or antistick property requires that the release web have a surface energy significantly lower than the surface tension of the masscoat. Silicone coatings meet this criterion.

### Origin

The organic and semiorganic adhesives may be classified according to origin as:

1. Natural: starch, dextrans, asphalt, animal and vegetable proteins, natural rubber, and shellac.
2. Semisynthetic: cellulose nitrate and the other cellulose, polyamides derived from dimer acids, and castor-oil based polyurethanes.
3. Synthetics:
  - (a) Vinyl-type addition polymers, both resins and elastomers: polyvinyl acetate, polyvinyl alcohol, acrylics, unsaturated polyesters, butadiene-acrylonitrile, butadiene-styrene, neoprene, butyl rubber, and polyisobutylene.
  - (b) Polymers formed by condensation and other step-wise mechanisms: epoxies, polyurethanes, polysulfide rubbers, and the reaction products of formaldehyde with phenol, resorcinol, urea, and melamine.

### Cure; Solubility; Crosslinking

Alternatively, adhesives may be categorized according to the solubility and fusibility of the final glue line:

1. *Soluble*, including *thermoplastic* (soluble and fusible): starch and derivatives, asphalts, some proteins, cellulose, vinyls, and some acrylics.
2. *Crosslinked* (insoluble and infusible): phenol- and resorcinol-formaldehyde, urea- and melamine-formaldehyde, epoxies, polyurethanes, natural and synthetic rubbers if vulcanized, anaerobics, and unsaturated polyesters.

The term “*thermosetting*” has been used traditionally for crosslinking compositions, even when they do not require elevated temperature to initiate the chemical reaction.

Crosslinking may involve the reaction of two chemically different intermediates, e.g.:

- (a) formaldehyde condensed with phenol, resorcinol;
- (b) formaldehyde condensed with urea, melamine;
- (c) isocyanate reacted with polyol to give polyurethane;
- (d) epoxide reacted with primary amine or polyamide-amine;
- (e) unsaturated polyester copolymerized with styrene;
- (f) sulfur-vulcanized diene rubbers.

Crosslinking may also take place among molecules of a single species, for example:

- (a) epoxide catalyzed by tertiary amine;
- (b) dimethacrylate compounded anaerobically so that it will polymerize when air is excluded;
- (c) peroxide-vulcanized rubbers.

Most adhesives which crosslink at room temperature are packaged in two containers, mixed just before use. The *moisture-curable* adhesives and sealants, however, are single-component compositions which have long shelf life as long as they are in closed containers, but react when dispensed and thus exposed to water vapor in the air. Among the growing roster of moisture-curable systems are three types of

sealants, as well as various adhesives:

- (a) *Isocyanate prepolymers*, made, e.g., by reaction of polyether polyol with an excess of aromatic diisocyanate, react with moisture to yield polyurethane-ureas. The concomitant formation of carbon dioxide gas is a drawback.
- (b) *Silicones* are made moisture-curable by blocking the end hydroxyls with easily hydrolyzable acetate groups. Consumer sealants of this type are recognizable by the acetic acid odor, when first applied.
- (c) *Polysulfide sealants* can be compounded with calcium peroxide or barium peroxide, which reacts with moisture to release hydrogen peroxide, which cures the polysulfide. Cure is slower than with the lead dioxide cure of two-component systems.
- (d) *Unsaturated polyesters* likewise utilize barium peroxide, plus a cobalt salt, as a latent catalyst system activated by moisture.
- (e) *Cyanoacrylates* polymerize spontaneously in the presence of basic catalysts, even with very weak bases such as water. Setting takes place within a few seconds after exposure to atmospheric moisture.
- (f) *Epoxy resins* can be compounded with ketimines which, on exposure to moisture, release amine curing agents. This technology, already used in coatings, may be applicable also to the adhesive bonding of porous substrates.

### Hybrids and Coupling Agents

Many adhesive-bonded compositions are hybrids, combining two types of groups. An important benefit of many types of hybrids is a non-Hookeian (nonlinear) stress-strain curve, with increased area under the curve (work to break), hence higher toughness, impact strength, and peel strength. Typically they have at least two  $T_g$ 's (glass transition temperatures), one below room temperature for the elastomeric component (providing good elongation), the other well above room temperature for the rigid component (providing good tensile

and compressive strength). The size range of hybrids is broad:

	Å
Composites	$10^4$ – $10^5$ and larger
Intermolecular	$10^2$ – $10^3$
Polymer blends	
Intramolecular	$10$ – $10^2$
Random copolymers	
Graft and block copolymers	
Other hybrids	

Among the more significant adhesive hybrids are:

1. *Neoprene (polychloroprene)-phenolics*: good "green" strength, adjustable open times, and high cured strength.
2. *Nitrile-phenolics*: excellent strength at high temperatures (but requires pressure because of evolution of water vapor).
3. *RFL (resorcinol formaldehyde resin plus latex)*: bonding of tire cord to rubber.
4. *Epoxy-nitrile*: metal bonds with high peel strength.
5. *EVA-wax-low molecular weight resin*: hot-melts for packaging, bookbinding, furniture edge-banding, etc.

*Coupling agents* are bifunctional hybrids designed to improve the adhesion between phases in composites and blends. Usually the disperse phase is inorganic, and the coupling agents accordingly consist of an organic functional group and an inorganic residue. The organic active site is utilized either to form a true chemical bond with the organic matrix, or at least to assure strong affinity to it, while the inorganic part reacts with or is absorbed by the reinforcement. Currently, the most popular types of coupling agents are of the silane type,  $X-R-Si(R')_3$ . The  $R'-Si$  bond is hydrolyzable.  $R'$  may be alkoxy, chloro, or acetoxy. The organic functional sites "X" are designed to match the polymer. Among these are amino and epoxide for bonding to epoxy resins as well as other polymers, and vinyl for bonding to unsaturated polyester.

One of the important adhesion problems which has received much attention but still remains not completely solved is the coupling of

some reinforcing fibers to thermosetting and thermoplastic matrix in *advanced composites*. While silanes work well on glass, bonding of graphite and aramid fibers could still be improved. Titanate coupling agents seem to work better on aramid than do silanes,<sup>58</sup> and graphite fibers are often sized with uncatalyzed epoxy resins when epoxy is used as composite matrix as well. However, new trends in advanced composites are toward heat-resistant thermoplastic matrices which could be even more difficult to couple with fibers.

### Adhesive Films

Both thermosetting and thermoplastic adhesives are available in film form. Films offer many advantages. They are uniform in both composition and thickness, convenient to handle, free from volatiles. But they are difficult to make, hence expensive; also, they require heat and pressure to achieve satisfactory bonds.

The largest volume film adhesive, polyvinyl butyral for safety glass, has been discussed above under the heading "thermoplastics." Another thermoplastic, pressure-sensitive acrylic, is the film material that is growing most rapidly. It is used to bond nameplates and trim on appliances, metal office furniture, machinery, etc.

The thermosetting films are employed for metal-to-metal bonding in aircraft, as well as less demanding appliance, electrical, and automotive requirements. These adhesives are hybrids designed to provide an optimum combination of shear strength, elongation, and heat resistance. Nitrile-phenolic and epoxy-nitrile are the leaders, followed by vinyl butyral-phenolic, epoxy-nylon, and epoxy-phenolic. The nitrile rubber in the epoxy-nitrile is a carboxyl-terminated butadiene-nitrile polymer which reacts with the epoxy at the elevated cure temperature.

### High Temperature Resistance; Flame Retardance

Resistance to prolonged exposure to high temperatures is required of some adhesives for the aircraft, aerospace, and electrical industries. Many less glamorous end uses—foundry molds and cores, coated and bonded abrasives, brake linings and other friction materials, and ther-

mal insulation—also demand binders with good heat resistance.

*Phenolics*, the oldest completely synthetic adhesives, perform well at elevated temperature, and are available at the low cost that is a necessity in the more mundane applications. The aromatic rings, the high crosslink density, and the resonance-intensifying hydroxyl groups all contribute to heat resistance as well as high shear strength. But cured phenolics still contain methylene linkages which provide sites for thermal degradation.

Where still more heat resistance is needed, we now have the *polyimides*, *polybenzimidazole*, *polyquinoxalines*<sup>53</sup> and other linear polymers in which the methylene content is reduced or eliminated. Conjugated unsaturation increases the thermal stability of these materials. Unfortunately, as the extent of condensation approaches that of the "ladder polymer" pyrones which might provide optimum heat resistance, the polymers become more intractable.

The type of polymer produced by condensing aromatic polyacids and polyamines depends on the functionality of the reactants:

Amine Functionality	Acid Functionality	Polymer
2	2	Polyamide (nylon)
2	3	Polyamide-imide
2	4	Polyimide
4	2	Polybenzimidazole
4	4	Pyrrone

*Flame retardancy* is a characteristic now required by the U.S. Government, under the Flammable Fabrics Act, of an increasing number of products including carpets, mattresses, automotive upholstery, and children's sleepwear. The lowest cost flame-retardant organic adhesives are *vinyl chloride polymers* plasticized with phosphate esters, and these are indeed being utilized for carpet backing and in the bonding of automotive fabrics. Ironically, some of the copolymers which were hailed in the early 1970's as answers to the Government's flame retardance regulations have later been withdrawn because they fail to meet the requirements of another Government agency, OSHA, for low content of vinyl chloride monomer, now branded a carcinogen.

Other flame-retardant adhesives contain vinylidene chloride latexes, halogenated epoxies, or additives such as diammonium phosphate or ammonium sulfamate. The epoxy resin derived from tetrabromo- or tetrachlorobisphenol A is used in special aircraft adhesives.

## MATCHING ADHESIVE TO ADHEREND

The adhesive and adherend must be compatible, if their union is to last.

When two materials are bonded, the resultant composite has at least five elements: adherent No. 1 / interface / adhesive / interface / adherend No. 2.

The strength of the adhesive joint will be the strength of its weakest member. If one of the adherends is paper, excessive stress will usually result in a "paper tear." With stronger substrates, however, the failure will be either *adhesive* at an interface or *cohesive* within the glue. Failure will not be at an interface if the adherend surface has been properly prepared and the adhesive wets the adherend and is otherwise appropriate. In other words, the adhesion between glue and substrate should be greater than the cohesion within the glue line. This will occur provided the combining of adhesive and adherend has caused a decrease in free energy, and provided also that excessive strains are not built up when the adhesive sets.

Let us consider the latter requirement first. Adhesives usually shrink as they harden. (Inorganic cements are exceptions.) Polymerization, the loss of solvent, even the cooling of a hot-melt may cause the glue line to contract. Strains are set up which induce the adhesive to pull away from the substrate. In addition, strains are produced when the adhesive joint is flexed. Various remedies may lessen the danger of failure from these causes:

1. Choose low-shrinking resins, e.g., epoxies rather than unsaturated polyesters.
2. Choose adhesives that are less rigid than the adherends; otherwise flexing will cause a concentration of stress in the glue line. (However, excessive flexibility in the adhesive may be accompanied by low cohesive strength.)
3. Keep the glue line as thin as possible, consistent with the smoothness of the adherends, if the stresses are chiefly tensile.

But porous adherends require the application of sufficient adhesive to avoid a "starved glue line." If the joint is to be exposed to considerable shear stress, the glue line should be somewhat thicker.

4. Incorporate inert and preferably inorganic fillers.
5. After applying the adhesive to an impervious substrate, evaporate water or solvents thoroughly before mating with a second impervious adherend.

In Chapter 3 of this Handbook, Gent and Hamed provide a comprehensive presentation of adhesion theory. Surface preparation is discussed by Mahoney in Chapter 4, and adhesives evaluation is examined in Rice's Chapter 5.

In this introductory chapter, we focus on two factors relating choice of adhesive to the substrate: *critical surface tension* and *solubility parameter*.

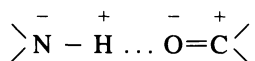
Let us examine the types of bonds that may exist between adhesive and adherend. These chemical bonds may be either primary or secondary.

*Primary* bonds include electrovalent, covalent, and metallic bonds. *Electrovalent* or *heteropolar* bonds may be a factor in protein adhesives. *Covalent* or *homopolar* bonds play a part in some finishing treatments for fiber glass. The *metallic* bond is formed by welding, soldering, and brazing. The metals and alloys involved are essentially high temperature thermoplastic adhesives, but are outside the scope of this volume.

By far the most important of the adhesive bonds are the *secondary* or *Van der Waals'* bonds that give rise to attraction between molecules. Most significant of these are the *London* or *dispersion forces*. They are responsible for virtually all the molar cohesion of nonpolar polymers such as polyethylene, natural rubber, SBR, and butyl rubber. These forces act at a distance of approximately 4 Å, and fall off rapidly, as the sixth power of the distance between atoms. Consequently, molecules must be in close proximity for London forces to be effective. This helps to explain why a very flexible molecule such as natural rubber is a better adhesive than a moderately flexible molecule such as polystyrene. Low modulus, indicating free-

dom of rotation of submolecules that permits the adhesive to conform to the adherend, is advantageous to adhesion.

*Interaction of permanent dipoles* results in strong bonds, especially if the positive dipole is an H-atom. The *hydrogen bond*, typified by



accounts for the excellent success with polar substrates of such diverse adhesives as starch and dextrin, polyvinyl alcohol, polyvinyl acetals, cellulose nitrate, phenolics, and epoxies. All of these adhesives contain phenolic or aliphatic hydroxyls. The carboxyl group, incorporated in small percentage in many vinyl-type polymers, is an even more powerful aid to adhesion. An entire chapter in this volume is devoted to carboxyl-containing elastomers. Among the adherends utilizing H-bond adhesives are wood, paper, leather, glass, and metals.

Two approaches, ostensibly different but in fact related, facilitate the selection of an appropriate adhesive to bond a specific substrate. In the Second Edition of this Handbook,<sup>19</sup> Zisman examines the influence of constitution on adhesion and demonstrates the usefulness of *critical surface energy* in determining which adhesives will wet a surface. In the present chapter, *solubility parameter* is discussed as a tool for predicting the compatibility of adhesive and adherend. Gardon<sup>34,35</sup> has pointed out the correlation between the two, which is borne out also in Table 1, in which some of the solubility parameters collected by Gardon and Burrell are compared with some of the critical surface tensions tabulated by Shafrin in the Second Edition.<sup>19</sup>

Figure 1 shows that, with increasing polarity and hydrogen bonding, the solubility parameter rises more sharply than the critical surface tension.

### Critical Surface Tension

In a series of classic investigations over a period of more than 25 years, Zisman and co-workers at Naval Research Laboratory examined the relationship between adhesion and chemical constitution. They determined the

critical surface tensions for spreading, with great precision, for well over one hundred polymers, from measurements of the contact angles with a variety of liquids whose surface tensions had been determined. The critical surface tension delineates the wettability of a solid surface, indicating the maximum surface tension desirable in an adhesive for a particular substrate.

Zisman showed that comb-shaped polymers with long fluoroalkyl side chains have the lowest critical surface energies, while hydrogen bonding polymers such as ureaformaldehyde, proteins and cellulose rank highest. To assure spreading and wetting, the fluid adhesive should have a surface tension no higher than the critical surface tension of the solid adherend.

### Solubility Parameter

When the substrate is organic and not too polar, the solubility parameter is useful in helping to select an adhesive.

If the bond between adhesive and substrate is to be strong, there must be a decrease in free energy as a result of combining the two. The free energy change on mixing two materials is:

$$\Delta F = \Delta H - T \Delta S,$$

where  $\Delta H$  is the heat of mixing and  $\Delta S$  is the entropy change. In general, when two materials are mixed, there is an increase in entropy; consequently the second term on the right of the equation is negative. If we can ignore the heat of mixing term, the free energy will also be negative. This tells us that materials will tend to combine provided the heat of mixing is not too high on the positive side. We see, also, that raising the temperature makes the entropy term more negative, thus aiding the process of combination. This is particularly true when at least one of the materials being mixed or combined is a high polymer.

The heat of mixing depends on the attractive forces between adhesive and adherend. These forces may be either primary or secondary bonds. If the heat of mixing is zero or if it is negative as the result of hydrogen bonding or other chemical combination of adherend and

**Table 1 Solubility Parameter and Critical Surface Tension**

	Solubility Parameter, $\delta$ hildebrands	Critical Surface Tension, $\gamma_c$ (dyn cm <sup>-1</sup> )
Poly(1H, 1H-pentadecafluorooctyl acrylate)	—	10.4
Polytetrafluoroethylene	6.2	18.5
Silicone, polydimethyl	7.6	24
Butyl rubber	7.7	27
Polyethylene	7.9	31
Natural rubber	7.9–8.3	—
Natural rubber-rosin adhesive	—	36
Polyisoprene, cis	7.9–8.3	31
Polybutadienè, cis	8.1–8.6	32
Butadiene-styrene rubbers	8.1–8.5	—
Polyisobutylene	8.0	—
Polystyrene	9.1	32.8
Polysulfide rubber	9.0–9.4	—
Neoprene (chloroprene)	8.2–9.4	38
Butadiene-acrylonitrile rubbers	9.4–9.5	—
Poly(vinyl acetate)	9.4	—
Poly(methyl methacrylate)	9.3	39
Poly(vinyl chloride)	9.5–9.7	39
Urea-formaldehyde resin	9.5–12.7	61
Epoxy	9.7–10.9	—
Polyamide-epichlorohydrin resin	—	52
Ethyl cellulose	10.3	—
Poly(vinyl chloride-acetate)	10.4	—
Poly(ethylene terephthalate)	10.7	43
Cellulose acetate	10.9	39
Cellulose nitrate	10.6–11.5	—
Phenolic resin	11.5	—
Resorcinol adhesives	—	51
Poly(vinylidene chloride) (saran)	12.2	40
Nylon 6,6	13.6	43
Polyacrylonitrile	15.4	44
Cellulose, from wood pulp	—	35.5, 42
Cellulose, from cotton linters	—	41.5
Cellulose, regenerated	—	44
Starch	—	39
Casein	—	43
Wool	—	45

adhesive, then wetting will surely be accomplished. For most nonpolar or moderately polar pairs of materials, however, the heat of mixing is positive; consequently the free energy will decrease only if this positive term is not too high.

Hildebrand<sup>22</sup> and others<sup>23–30</sup> utilized the concept of *solubility parameter*,  $\delta$ , to show why some pairs of materials mix more readily than others. The solubility parameter is related to the *internal pressure* or *cohesive-energy density*:

$$\delta = (\Delta E/V)^{1/2}$$

where  $\Delta E$  = the energy of vaporization, and  $V$  = the molar volume.

The term,  $\Delta E/V$ , the energy of vaporization per cc, is called the *internal pressure* or *cohesive-energy density*. Its square root, the solubility parameter, is termed the “hildebrand.”

For liquids such as the fluorocarbons and hydrocarbons, this energy is very low; therefore low molecular-weight materials of these compositions have very low boiling points. The low molecular-weight fluorocarbons were thus used in aerosol dispensers, until it was realized that



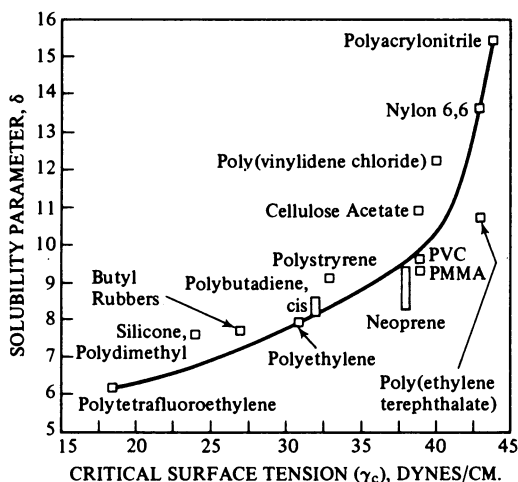


Fig. 1. Critical surface tension vs. solubility parameter.

they adversely affect the ozone layer; and low molecular-weight hydrocarbons are the main constituents of natural gas.

As soon as we incorporate polar groups, we find that it requires more energy to vaporize a molecule, i.e., to separate it from its companions. Thus, acetone has a higher boiling point than butane, and isopropyl alcohol is still higher, although all three molecules are approximately the same size and weight.

Hildebrand indicated that the greater the difference between the solubility parameters of the two materials, the greater the (positive and undesirable) heat of mixing.

$$\Delta H = V(\delta_1 - \delta_2)^2 \phi_1 \phi_2$$

where  $V$  = the total volume, and  $\phi_1$  and  $\phi_2$  = the volume fractions of the respective components. Consequently, combination is most likely to take place when adhesive and adherend are most alike in solubility parameter. Furthermore, the composite is most likely to resist the intrusion of another material (for example, water) when solubility parameters are close together.

Solubility parameter theory was advanced first by Hildebrand and Scott.<sup>30</sup> Small<sup>31</sup> developed a method for calculating the parameters from the contributions of groups within the molecule. Burrell,<sup>32</sup> Hansen,<sup>36,38</sup> and Crowley et al.<sup>37</sup> were especially successful in utilizing the concept for the formulation of solvent-based

coatings; and Skeist<sup>33</sup> applied it to the selection of adhesives for plastics. Gardon<sup>34,35</sup> has provided a comprehensive review of the voluminous literature. See also Chapters on Thermoplastic Rubbers, Neoprene, and Bonding Plastics.

Burrell attributed some discrepancies between theory and fact to *hydrogen bonding*, and Hansen and Crowley added *dipole moment* as still a third parameter which should be similar in the two materials being brought together. These two characteristics do not necessarily operate in parallel. Thus, for example, dioxane has high hydrogen bonding but almost no dipole moment, while ethylene carbonate combines a more moderate hydrogen bonding with high dipole moment.<sup>37</sup>

	Solubility Parameter	Hydrogen Bonding	Dipole Moment
Dioxane (1, 4)	9.9	9.7	0.4
Ethylene car- bonate	14.7	4.9	4.9

The solubility parameter of a polymer cannot be measured directly, as polymers are not volatile. It can be calculated from Small's molar attraction constants, but preferably it is inferred from the solubility parameters of solvents having maximum solubilizing or swelling action.

Table 1 shows good correlation between solubility parameter and critical surface tension for polymers at the low end of both scales. With increasing values, however, anomalies become apparent, e.g., for amino resins and urea formaldehyde, poly(ethylene terephthalate), and cellulose from different sources. The discrepancies can be attributed at least partly to differences in crystallinity, the presence of compounding ingredients, and differences in chemical composition of the bulk polymer from the surface. Surface treatment of *polyethylene*, whether by flame, liquid oxidants, electron bombardment, or ionic bombardment, creates carboxyl groups and other oxygen-containing moieties which raise the surface energy, allowing the treated polyethylene to accept printing inks and polar adhesives which would otherwise not wet the polymer. Where solubility pa-

rameter and contact angle measurements disagree, therefore, the latter provide the better direction for choosing adhesives, provided they have been carried out on the materials as actually prepared for bonding.

Frequently it is necessary to combine materials having quite dissimilar solubility parameters, and often differing in modulus as well. An important example, the manufacture of tires, is discussed in the chapter, "Bonding Textiles to Rubber." Use is made of a hybrid adhesive, RFL, containing heat-resistant resorcinol-formaldehyde for good attachment primarily to the polar, high modulus fiber, plus an elastomer of moderate solubility parameter, butadiene-styrene-vinyl pyridine terpolymer latex, mainly for the rubber.

Table 2 prepared by Reinhart and Callomon<sup>59</sup> is a succinct tabulation of adhesives suitable for combining either similar or different substrates.

## DESIGNING POLYMERS FOR ADHESIVES

Advances in polymer chemistry and technology have led to a variety of new polymers, hybrids, copolymers, etc., presenting the adhesive formulator with a wide choice of materials. Many approaches to synthesis are available:

- Grafting
- Block copolymerization
- Reactive oligomers
- Interpenetrating networks
- Copolymerization with functional monomers

When the adhesives are crosslinked by curing agents, the design also includes the type of crosslinker, accelerator, etc. Intermolecular reactions between the polymer base and modifying resins, e.g., neoprene and phenolic resin, impart stability and non-separation properties to the adhesives formulae. And, when the composition includes inorganic fillers or reinforcement, chemical linkage is constructed through a *coupling agent* which ties the matrix polymer to the inorganic surface.

### Grafting

Polar monomers are grafted onto polyolefins in order to improve the adhesion properties of the latter. This technique is used, for example, with polypropylene and polyethylene resins for extrusion coating and hot-melt adhesive applications as well as for resin grades reinforced with glass. The grafted monomers are usually either acrylic acid or maleic anhydride. Carboxyl groups introduced in this manner provide increased adhesion to glass or mineral fillers in molding resins, as well as better coupling to aluminum foil, paper, and other substrates in extrusion-coated products.

### Reactive Oligomers and Polymers

This approach is already utilized widely in radiation-cured adhesives, urethane and epoxy adhesives, and other areas. Here an oligomer of a particular type, e.g., polyurethane, is terminated with functional groups which are subsequently exploited to extend the polymer chain or to crosslink the system. Examples of commercial materials include:

Polymer Backbone	Functional End Groups	Use
Urethane	Acrylate	Radiation cure
Epoxy	Acrylate	Radiation cure
Silicone	Acrylate	Radiation cure
Polyether	Isocyanate	Urethane adhesives
Polyester	Isocyanate	Urethane adhesives
Polybutadiene	Carboxyl	Rocket fuel binders
Polyimide	Ethynyl	Heat resistant adhesives
Polyimide	Nadic	Heat resistant adhesives
Polybutadiene	Hydroxyl	Urethane adhesives
Butadiene-acrylonitrile	Amine	Epoxy adhesive hardeners
Polystyrene ("Macromer")	Methacrylate	Hot melt pressure-sensitives



Adhesive number code for Table 2:

Thermoplastic	Thermosetting	Elastomeric	Resin Blends
(1) Polyvinyl acetate	(11) Phenol formaldehyde (phenolic)	(21) Natural rubber	(31) Phenolic-vinyl
(2) Polyvinyl alcohol	(12) Resorcinol, phenol-resorcinol	(22) Reclaim rubber	(32) Phenolic-polyvinyl butyral
(3) Acrylic	(13) Epoxy	(23) Butadiene-styrene rubber	(33) Phenolic-polyvinyl formal
(4) Cellulose nitrate	(14) Urea formaldehyde	(24) Neoprene	(34) Phenolic-nylon
(5) Asphalt	(15) Melamine, melamine-urea formaldehyde	(25) Buna-N	(35) Phenolic-neoprene
(6) Ocoresin	(16) Alkyd	(26) Silicone	(36) Phenolic-butadiene-acrylonitrile rubber

## Copolymerization

A variety of functional monomers can be distributed throughout the polymer chain, usually in random fashion, to impart specific properties at relatively low incorporation level. Though usually more expensive on a per pound basis than the monomer which is the major component of the copolymer, they offer high cost effectiveness. Many examples can be offered. *Allyl ureide*<sup>56,57</sup> monomers have been incorporated as adhesion-promoting moieties in architectural latex paints at levels as low as 1% or less to provide wet adhesion to the substrate. Similar benefits were obtained from such monomers as *dimethyl-t-butylaminoethyl-methacrylate*, *aminoalkyl methacrylate*, and *ethylene imine*, though the latter, because of its carcinogenicity, is no longer produced in the U.S. *Acrylic acid* and other organic acids (methacrylic, fumaric, crotonic) are introduced during polymerization of ethylene and propylene to provide adhesion to metal and other polar substrates.

An interesting modification involves *expandable monomers*. These materials, synthesized by Dr. William J. Bailey and coworkers at University of Maryland, are *spiro monomers*, double rings which open and expand on polymerization.<sup>61,62</sup> They can be useful in adhesives which are based on polymer/monomer solution, such as "structural" acrylics, radiation-cured acrylates, etc. These monomers can counteract shrinkage on curing, which is detrimental to adhesion.

*Crosslinking* is an additional task for comonomers. *N-methylol acrylamide* fulfills this function in acrylic, vinyl acetate and styrene-butadiene latexes for textile binding. *Glycidyl methacrylate* can crosslink through reaction of its epoxide moiety with carboxyl or amino groups. *Isocyanatoethyl methacrylate*<sup>54</sup> contains a reactive isocyanate group; there are many others.

## Block Copolymers

Synthesis of these has led to the development of thermoplastic elastomers, useful especially in hot-melt pressure-sensitive adhesives. Polymers with two glass transition temperatures have been developed which are elasto-

meric at ambient temperature but become fluid at elevated temperatures. Typical examples are styrene-isoprene-styrene or styrene-butadiene-styrene block copolymers with their "soft" midblocks (low  $T_g$ ) and "hard" end blocks, and their hydrogenated modifications, styrene-ethylene-butylene-styrene.

### Interpenetrating Polymer Network (IPN)

IPN<sup>55</sup> is a new approach to the synthesis of polymers. While still mostly in the investigative rather than the commercial stage, IPNs could become an important tool in designing adhesives. The IPNs are crosslinked or semi-crosslinked systems, composed usually of two types of three-dimensional polymer networks interlocked with each other. This permits the coupling of two dissimilar polymers with widely disparate glass transition temperatures, solubility parameters, polarities, etc. A two-glass transition temperature system of that type could also be useful in pressure-sensitive adhesives and other applications where different elastic properties are needed at ambient and at elevated temperatures. The dual glass transition pattern also leads to high energy absorption characteristics, and adhesives based on polymers of that type could be important in energy absorbing devices—acoustical, crash pads, etc. Another goal could be improved toughness when a high glass transition temperature, high modulus adhesive with low elongation is "married" to a low modulus elastomer such as a silicone.

### NEW TRENDS

Many trends in polymer synthesis generally are being applied, or could be applied in the future, to adhesives. There is a continuous stride toward polymers with superior *heat resistance*. To achieve this, various heterocyclic and aromatic structures are built into polymers, e.g., by intramolecular cyclization (polyimides, polybenzimidazoles), trimerization of terminal acetylene or nitrile groups, etc. Another route is to introduce highly stable perfluorinated units into the polymer. While heat-resistant polymers find their main applications as laminating

resins, heat-resistant adhesives are in demand as well.

Some developments for non-adhesive purposes could serve as a starting point to improve adhesives as well. For example, *superabsorbents*, polymers which soak water avidly, could become a basis for adhesives to be applied on wet surfaces. Other polymers could be developed to have similar affinity to oil, hence to be useful for application on oily substrates.

*Conductive polymers* are the subject of extensive research at many universities and industrial research centers. If successfully commercialized, they could become a starting point for conductive adhesive formulations and eliminate the need for the costly silver fillers used now. These polymers are likely to be based on delocalized electron structures such as conjugated double bonds, wholly aromatic polymers, and the like.

*Crosslinkers and Accelerators.* Besides the polymers themselves, changes and improvements are taking place in curing agents, hardeners, catalysts, and polymer modifiers. For example, if epoxy adhesives with improved heat resistance are needed, the hardeners can be aromatic anhydrides and amines such as benzophenone tetracarboxylic dianhydride, pyromellitic dianhydride, diaminodiphenyl sulfone. To enhance curing speed, epoxy systems utilize mercaptan hardeners, while acrylic monomer/polymer blends avail themselves of amine/aldehyde catalysts with benzosulfimide (saccharin) accelerators. *Radiation-curing* systems for today and tomorrow utilize both visible light and laser beams.

*Toxicity.* While many new materials are added to the adhesive chemist's arsenal, some are being removed as well. Compounds which cause health and environmental concern include ethylenimine, methylene-*bis*(*o*-chloroaniline) (MOCA), hexamethylene diisocyanate, formaldehyde. Some systems are no longer in use; in others, modifications have been made. Thus radiation-curing technology is replacing some types of multifunctional acrylate monomers with alkoxylated compounds, because the latter are less irritating and less toxic. An example is trimethylolpropane triethoxy triacrylate.

*Theoretical Developments.* Advances in

polymer theory have their applications also in research on the phenomena of adhesion. Adsorption at the interface, diffusion, and other subjects related to adhesion have been investigated through a scaling approach which uses mathematical models taken from physics (ferromagnetism theory) to explain the random walk behavior of polymer molecules.<sup>39-41</sup> Studies of kinetics of wetting include work by de Gennes<sup>42</sup> and Cazabat.<sup>43</sup> Electrostatic adhesion theory was developed in the 1970s by Derjagin.<sup>44</sup>

*Analytical methods* to probe adhesion have also advanced. Dynamic mechanical analysis methods have been found especially useful in investigating the cure process of epoxy resins and in research on pressure-sensitive formulations. Widely used is *torsional braid analysis* (TBA).<sup>48,49</sup> Surface investigation avails itself of *electron spectroscopy for chemical analysis* (ESCA).<sup>50</sup> Other investigative approaches to following the cure of epoxies include dielectric spectroscopy<sup>51</sup> and viscosity-dependent fluorescent probe.<sup>52</sup>

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## 2

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# The Role of Adhesives In the Economy

ARNOLD BRIEF

*Skeist Incorporated*

*Consultants to the Polymer Industries*

*Whippany, New Jersey*

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In the quarter century between publication of the first and third editions of *Handbook of Adhesives*, the adhesives industry has shown exciting development and diversity. It has grown from 3 billion pounds worth \$650 million in 1962 to over 10 billion pounds valued at \$5.5 billion in 1987. This chapter will concentrate on the contributions made by adhesives to industrial growth in the United States since the second edition of this Handbook, reviewing both the types of adhesives and applications employed by the adhesive-using industries.

In 1975, these industries consumed about 7 billion pounds of compound valued at 2.2 billion dollars. A dozen years later, the business had grown to 10.5 billion pounds worth \$5.5 billion (see Table 1).

While overall adhesive consumption increased 250% during the last 25 years, synthetic compounds (thermoplastic, thermoset, and elastomer) grew by more than 600%. In

1975, about 75% of adhesive tonnage was based on synthetic materials; by 1987, the share had climbed to 83%. Synthetic adhesives provided improved adhesion to a variety of substrates, can be applied at faster speeds, exhibit superior properties and have contributed to new, challenging product designs (Tables 2-6).

### THE "BIG SEVEN" RAPID GROWTH ADHESIVES

Although overall adhesive volume increased by 50% in the 1975-87 period, there were seven adhesive materials that experienced growth of at least 100%. These high performers are: acrylics, cyanoacrylates, anaerobics, polyvinyl acetate, ethylene-vinyl acetate, styrenic block copolymers, and polyurethanes (Tables 7 and 8).

**Table 1. Growth of Adhesives.**

	MM lbs.	\$ MM	Average Annual Growth Rate, %	
			(lbs.)	(\$)
1975	7000	2200		
1987	10500	5500	3.5	8



**Table 2. Market Share by Adhesive Type.**

	1975		1987	
	% (lbs.)	% (\$)	% (lbs.)	% (\$)
Thermoplastic	37	35	44	40
Thermosetting	35	35	33	27
Elastomers	7	18	8	24
Natural and others	21	12	15	9

**Table 3. Thermoplastic Adhesives.**

<i>Major Markets</i>	<i>Key Adhesives</i>	<i>Leading Applications</i>
Construction	PVAC	Gypsum board
Textile	C-SB	Carpeting backing
Packaging	PVAC, EVA	Case sealing/assembly, folding carton sealing/assembly

**Table 4. Thermosetting Adhesives.**

<i>Major Markets</i>	<i>Key Adhesives</i>	<i>Leading Applications</i>
Wood bonding	UF, PF	Particleboard, plywood
Construction	PF, VF, Epoxy	Glass fiber, asphalt roofing, concrete
Foundry	Phenolics	
Auto Aftermarket	Unsaturated polyester	Body patching

**Table 5. Elastomeric Adhesives.**

Construction	SBR	Carpet installation, vinyl flooring installation, ceramic tile
Pressure-sensitive	Natural rubber, SIS block copolymer, Butyl	Tapes, labels

**Table 6. Natural and Other Types of Adhesives.**

<i>Major Markets</i>	<i>Key Adhesives</i>	<i>Leading Applications</i>
Construction	Starch, Asphalt	Gypsum board binders, roofing tiles
Packaging	Starch	Corrugated board

**Table 7. High Achievers.**

	% Increase 1975-89 (lbs.)
Acrylics	175
Cyanoacrylates	500
Anaerobics	250
Polyvinyl acetate	100
Ethylene-vinyl acetate	150
Styrenic block copolymers	800
Polyurethanes	450

**Table 8. High Achievers as a Percentage of Total.**

	1975		1987	
	% (lbs.)	% (\$)	% (lbs.)	% (\$)
"Big 7"	18	24	27	33

## Acrylics

These are multifaceted polymers that are utilized in a variety of applications and in many forms: emulsion, solvent solution, 100% reactive, radiation-cured, and film. In the last dozen years, consumption of acrylic adhesives jumped 175%. Construction and pressure-sensitives accounted for most of this increase. In the former, acrylic latexes are making inroads on the territory held by SBR adhesive. In pressure sensitives, the acrylics (latex, solution, and radiation cured) make up one-third of the polymer demand. In this segment, acrylic latexes grew by ten times during the last twelve years. Acrylic solutions, used for making tapes and labels, are usually applied to film substrates.

A third major outlet for acrylics is textiles, mainly for nonwovens and flocking adhesives. Other markets include packaging, automotive, electrical/electronic, abrasives, furniture, etc.

In *construction* applications, acrylic adhesives showed a spectacular 15- to 20-fold increase. In 1975, the predominant outlet was concrete binders; but by 1987 acrylics were being employed in significant quantities for installation of ceramic tiles, decorative bricks and stones, carpeting, as a binder for cellulose insulation, and in concrete binders and adhesives. These applications account for about 90% of acrylic adhesives in construction.

Acrylic *textile* adhesives are still leaders as binders for nonwovens and fiberfill, but they have lost much ground to the less expensive vinyl acetate copolymers. Flocking continues to be a solid market for acrylics.

*Pressure-sensitive* adhesives based on acrylic polymers grew 3.5-fold in the last dozen years. The acrylics are mostly emulsions and solutions, plus small quantities of radiation-curable systems. In tapes, acrylic adhesives are applied mainly to non-paper substrates such as polypropylene, acetate, cellophane, and polyester. In labels, acrylics are used for making permanent paper labels and plastic labels.

In *packaging*, acrylics have begun to penetrate the film laminating field. Water-based acrylics are the fastest-growing film-to-film laminating adhesive. However, these water-based compounds are slower-drying and less attractive than solvent-based or 100% solids systems.

Small amounts of acrylic adhesives are utilized by *automotive* manufacturers, the largest application being headliners. This application, which consists of polystyrene board bonded with acrylic adhesives, is being replaced by fiberglass headliners bonded with SBR acrylics. Another outlet for acrylics is bonding vacuum-formed parts.

In the *electrical/electronic* market, acrylic film adhesives are applied to flexible printed circuits. Radiation-curable acrylates are employed as laminating adhesives (*furniture*) and binders for *coated abrasives* (Table 9).

## Cyanoacrylates

This "miracle glue" was introduced in 1959. It took about 10–15 years for the adhesive to enter the steep growth stage of its life cycle. The Consumer Product Safety Commission considered suspending its distribution to the consumer market because of the material's excellent adhesion to skin; but the Commission finally decided that a warning label as required under the Hazardous Substances Act would be sufficient. Since 1975, consumption has jumped six-fold, and consumer applications have swelled from less than 20% of the total volume to over 40%. Other major outlets include electronics, toys and hobbies. Cyanoacrylates are now reaching maturity, and future growth will be more moderate (Table 10).

## Anaerobics

Initially anaerobic adhesives were used mainly for threadlocking of screws, nuts, and bolts. Since 1975, consumption increased 3.5 times; but as the main applications have matured, future growth potential is not as great. Automotive is the largest outlet for anaerobics; other uses include machine assembly, electrical product assembly, maintenance, repair, etc. (Table 11).

## Polyvinyl Acetate

PVAC (the term embraces both homopolymer and copolymers) was in the forefront of the transition of adhesives from natural to synthetic adhesives. While overall consumption of homopolymer plus copolymer doubled in the 1975–87 period, the copolymer adhesives in-

**Table 9. Acrylic Adhesives.**

<i>Application</i>	<i>Function/End Use</i>
Construction	
Ceramic tile	Installation
Decorative brick	Installation
Concrete	Polymer cements, bond coats, and admixture to concrete
Cellulose insulation	Binder for fibers and adhesive to substrate
Carpeting	Installation
Core base	Installation
Asphalt roofing	Additive to urea-formaldehyde resin
Studs and framing	Interior
Wall covering	Installation
Glass fiber and rockwool insulation	Lamination
Ceiling tiles	Installation
Textile	
Nonwovens	Diaper, medical, apparel interlining
Fiberfill	Apparel
Flocking	Apparel
Laminating	Fabric/polyurethane foam
Tie Coats	Polyurethane-coated fabric
Pressure Sensitive	
Tape	Packaging, office, nameplates, medical
Labels and decals	Permanent labels, removable labels, freezer labels, plastic labels
Packaging	
Film to film	
Film to paper	
Foil to paper	
Automotive	
Headliners	
Vacuum-formed parts	
Threaded component compounds	
Electrical/Electronic	
Flexible printed circuits	
Magnet bonding	
Die attachment	
Abrasives	
Coated abrasives	
Furniture	
Paper or vinyl film lamination	Kitchen cabinets, residential furniture

**Table 10. Cyanoacrylate Adhesives.**

<i>Application</i>	<i>Function/End Use</i>
Consumer	Fast bonding applications
Electronics	Speaker magnet bonding, printed-circuit boards
Automotive	Engine rubber mounting, shock absorbers, rubber bonding
Toys and Hobbies	Bonding parts of dolls and rubber toys
Cosmetic Containers	Lipstick holders, bonding mirrors in compact cases
Appliances	Attaching trim, bonding internal devices
Artificial fingernails	Attaching
Maintenance, repair	Metal-to-metal, rubber bonding, locking parts

**Table 11. Anaerobic Adhesives.**

<i>Application</i>	<i>Function/End Use</i>
Automotive	
Porosity sealants	Prevent failure of engine block
Threaded fittings	
Flange sealants	Formed-in-place gaskets
Retaining compounds	
Threadlocking	
Rearview mirror	Installing
Maintenance, Repair, Overhaul	
Structural Bonding	

creased by a dramatic 250%. The preferred comonomers are ethylene and acrylate esters. Three outlets for PVAC, packaging, construction, and textiles, account for 80% of the polymer and 95% of the compound.

PVAC adhesives are found in a dozen *construction* applications. The largest is ready-mix joint cements for gypsum board. These are highly filled formulations with a polymer content of only 3%. Concrete adhesives containing PVAC serve to bond new concrete to old. Vinyl acetate-ethylene is the material of choice for vinyl and paper lamination to hardboard, gypsum board, and other substrates. Installation of vinyl flooring may be accomplished with PVAC adhesives.

In *packaging*, PVAC formulations have been the material of choice for over 25 years, and they have increased by 140% in the last 12 years. In spite of its higher cost, PVAC was preferred over starch and dextrin for more demanding applications because of its strength, setting speed, adhesion and ease of compounding. (Starch retains its huge market in corrugated board.) PVAC has some 25 packaging applications with the bulk of the tonnage for case sealing/assembly, carton sealing/assembly and envelopes.

The largest portion of PVAC adhesives in textiles is a binder for nonwovens and fiberfill. Here the rise in consumption was more than eight-fold as a result of the successful penetration of vinyl acetate-ethylene and vinyl acetate-acrylate copolymers.

As a *furniture* adhesive, PVAC is used for general assembly applications, film overlay and high pressure lamination, edge gluing, wood

veneer, and edge bonding. The demand increased by 200% in the last dozen years.

In the *consumer* sector, "white glue" continues to be a staple for both home and shop.

Consumption of PVAC *bookbinding* adhesive almost doubled during the past 12 years, mostly for the casing-in step in edition books and for making continuous business forms (Table 12).

### Ethylene-Vinyl Acetate Copolymers

Consumption of EVA *hot melt* adhesives increased 150% during the 1975–87 period. More than one-half of the EVA adhesive volume goes into packaging, and EVA accounts for about two-thirds of the total demand for hot melt adhesives. Another one-third of the poundage is distributed among three applications: textile, disposables, and bookbinding.

EVA hot melts are found in some 15 *packaging* applications. About 85% of the total is for case and carton sealing. Other markets which consume significant amounts of EVA adhesives include: automotive carpeting, assembly of disposable diapers, perfect binding (bookbinding), edge banding, film overlay, and general assembly of furniture (Table 13).

### Styrenic Block Copolymers

These thermoplastic elastomers experienced a dramatic nine-fold increase during the 1975–87 period, resulting from a veritable explosion in usage as pressure sensitive adhesives.

Before the 1970s, the pressure sensitive industry was employing solvent-based systems made from SBR or natural rubber. About two decades ago, hot melt pressure sensitive adhesives based on styrenic block copolymers (mainly styrene-isoprene-styrene) and acrylic emulsions were introduced. The reason for these technological developments was to decrease the dependency on solvents. Today hot melts account for about 20% of the pressure sensitive adhesive volume, up from less than 10% in 1975.

Styrenic block copolymers serve as mass-coats for pressure sensitives, mainly tapes. They are applied mostly as hot melts but also from solution.

**Table 12. Polyvinyl Acetate Adhesives.**

<i>Application</i>	<i>Function/End Use</i>
Construction	
Gypsum board joint cement	
Concrete	
Paper and film lamination	
Vinyl flooring	
Wood doors	
Glass fiber insulation	Bonding facing to fibers
Ceramic tile	Installation
Mobile homes	Assembly
Packaging	
Case	Assembly, sealing
Carton	Assembly, sealing
Tray forming	Assembly
Set-up boxes	Assembly
Bags	Heavy-duty, specialty, mailer
Envelopes	
Gummed products	Tape, paper
Laminations	Paper-paperboard, film-film, foil-paper, film-paper
Tubes and cores	
Composite cans	
Labeling	Plastic bottle, can
Paper cups and tubes	
Cigarette making	
Textile	
Nonwovens	
Fiberfill	
Carpeting	
Tie coats	
Flocking	
Furniture	
General purpose	
Laminations	Film overlay, high pressure
Wood veneer	
Edge gluing	
Edge bonding	
Consumer	
General purpose	
Bookbinding	
Edition books	Casing-in
Softcover	
Magazines	Primers
Business forms	
Other	
Disposables	
Pencils	
Paint rollers	

Other outlets for styrenic block copolymers which were developed during the last decade include: assembly of diapers, adhesives for

plastic beverage bottles (cup and labeling), installing automotive carpeting, bookbinding (Table 14).

**Table 13. Ethylene-Vinyl Acetate Adhesives.**

<i>Application</i>	<i>Function/End Use</i>
Packaging	
Case	Sealing, assembly
Carton	Sealing, assembly
Tray	Assembly
Labeling	Plastic bottle, can, glass bottle
Fiber drums	Assembly
Composite cans	Assembly
Mailer bags	
Cigarette making	
Textile	
Carpeting	Automotive
Disposables	
Diapers, others	Assembly
Bookbinding	
Edition books	Perfect binding, lining
Softcover books	Perfect binding
Magazines	
Directories	
Catalogues	
Furniture	
Edge banding	
Film overlay	
General assembly	
Consumer	
Hobbies	
Automotive	
Sound-deadening pad	Installation
Sponge-to-metal	Bonding
Filters	
Air filters	
Construction	
Carpet seaming tape	
Footwear	
Box toe, counters	
Shank attaching	

### Polyurethane

The major markets for polyurethane adhesives are textiles, forest products, and packaging. The first two applications were developed only during the past decade. Consumption of polyurethane adhesives increased by 450% in the 1975–87 timespan. Carpet backing adhesives was the largest segment credited with this remarkable growth.

Almost one-half of polyurethane adhesives is

**Table 14. Styrenic Block Copolymers.**

<i>Application</i>	<i>Function/End Use</i>
Pressure Sensitive	
Tapes	
Labels	
Disposables	
Diaper	Assembly
Packaging	
Cup, labeling	Plastic beverage bottles
Automotive	
Carpeting	Installation
Bookbinding	
Edition books	Perfect binding
Magazines	

consumed in textile applications, mainly carpeting. Carpets backed with polyurethane go into both residential and contract (i.e., commercial) installations.

Polyurethanes are used in patching compounds for softwood plywood. In packaging, polyurethanes are utilized primarily as laminating adhesives, mainly in film-to-film constructions.

The principal applications for polyurethane adhesives in construction include mobile homes, modular homes, thermal sandwich panels. In automotive vehicles, polyurethanes serve to bond FRP (fiber-reinforced plastics) and vacuum-formed ABS/PVC door panels.

Film overlay laminations (furniture) and sole attaching (footwear) are other applications for polyurethane adhesives (Table 15).

### THE ADHESIVE-USING INDUSTRIES

Adhesives form an integral part of myriad fabricated products. The cost contribution of adhesives is usually small, so that the end user does not pay too much attention to them. But, when they don't work, damages can be severe.

Adhesives serve in the manufacture of motor vehicles, aircraft, appliances, electrical/electronic components, homes, bonded wood, furniture, carpets, books, shoes, and even baby diapers. Historically, most of the volume has been devoted to the bonding of three porous substrates: wood, paper, and textiles. Future

**Table 15. Polyurethane Adhesives.**

<i>Application</i>	<i>Function/End Use</i>
Textile	
Carpet	
Tie coats	
Labels and emblems	
Forest Products	
Plywood patching	
Packaging	
Film to film	
Film to foil	
Film to paper	
Construction	
Mobile homes	Installation of gypsum
Modular homes	board ceilings, thermal
Panels	sandwich
Glued plywood floors	
Automotive	
FRP panel bonding	
Vacuum-formed door panels	
Furniture	
Vinyl overlay lamination	To boardstock, metal
Footwear	
Sole attaching	

growth opportunities, however, are in bonding non-porous substrates, e.g., plastic, metal, rubber, glass, etc.

**Construction**

Adhesives are utilized in construction for many structural and decorative applications, e.g., for installing vinyl flooring, carpeting, ceramic tile, wallcovering, making doors, gluing floors, etc. The construction industry is one of the largest outlets for adhesives, requiring some 40 types of adhesives in about 30 different applications. The bulk of the volume consists of thermoplastic, water-based adhesives (Table 16).

**Forest Products**

Wood bonding is one of the largest markets for adhesives. Plywood, particleboard, fiberboard, and other wood products involve mainly thermosetting and water-based adhesives, espe-

cially phenol-formaldehyde and urea-formaldehyde (Table 17).

**Furniture**

Adhesives enter into the manufacture of both residential and commercial wood and metal furniture, including office furniture, countertops, vanities, stereo speakers, TV cabinets, kitchen cabinets. More than a dozen types of adhesives are employed; PVAC is the largest (Table 18).

**Automotive**

Some 25 types of adhesives are utilized in the assembly of cars. The typical vehicle contains about 20 lbs. of adhesives. About two-thirds of the poundage goes into engineering/structural applications. Among the high-volume uses are the bonding of hood and deck lids (PVC plastisol), safety glass (polyvinyl butyral film), and tires (resorcinol-formaldehyde latex.) During the last dozen years, a number of new adhesive applications were developed, and the future for certain applications such as bonding of FRP components is bright (Table 19).

**Aircraft**

This industry does not use large quantities of adhesives. However, the products are expensive, as they are highly specialized and must meet strict specifications. The adhesives are utilized for both structural and nonstructural applications. Indeed, aircraft is the single most well-defined market for engineering/structural adhesives. The most common application is for epoxy hybrid films to bond metal structures (Table 20).

**Electrical/Electronic**

A variety of expensive materials are required in small volumes for electrical/electronic applications. Their average price is almost 20 times greater than the average for all adhesives. Conductive adhesives are the most costly. Electrical/electronic adhesives must exhibit good electrical, bonding, and mechanical properties (Table 21).

**Table 16. Construction Adhesives.**

<i>Application</i>	<i>Adhesive</i>	<i>Function/End Use</i>
Gypsum board	PVAC	Joint cement
	Starch	Binder
Concrete	Epoxy	Adhesives
	PVAC	Adhesives/additives
	Acrylic	Adhesives/additives
	SBR	Additive
Carpeting	SBR	Installation
	Acrylic	Installation
	Neoprene	Installation
	Natural Rubber	Installation
Recreational surfaces	PUR	Installation
Artificial turf	SBR	Installation
	PVAC	Installation
	Acrylic	Installation
Glass fiber and rock wool insulation	Phenolic	Binding glass fiber together
	Asphalt	Bonding of fibers to facing
	Neoprene	
	PVAC	
	PVDC	
	PE	
	PP	
	EVA	
	PVDC	Laminating plies of facing
	Neoprene	
	Sodium silicate	
	Acrylic	
	PVAC	
Roofing	Asphalt	Installation of vapor barriers and insulation board for roofing
	SBR/asphalt	
	Neoprene	Bonding single-ply membranes
	Butyl	
Ceiling tiles	Rosin	Installation
	Acrylic	
Ceramic tile	SBR	Mortars and Grouts
	Acrylic	
	Epoxy	
	Furan	
	Silicone	
Ceramic tile	SBR	Additives to cement
	Acrylic	
	PVAC	
	PVA	
Stud and framing	SBR	Installing gypsum board, plywood, and paneling over wall studs
	Neoprene	
	Acrylic	
Wallcovering	Dextrin	Installation
	Starch	
	Acrylic	
	Carboxymethyl cellulose	

(Continued on page 30)



**Table 16. (Continued)**

<i>Application</i>	<i>Adhesive</i>	<i>Function/End Use</i>
Vinyl flooring	Asphalt	Installing vinyl tile
	PVAC	
	Epoxy	
	SBR	Installing vinyl sheet
	SBR	
	PVAC	
Pipe-joint cements	Linoleum paste	Joining PVC pipe
	Epoxy	
	PVC	
	ABS	
Doors	CPVC	Joining ABS pipe
	Casein	Joining CPVC pipe
	PVAC	Wood bonding
	UF	
Safety glass	Neoprene	Metal bonding
	Epoxy	
	PVB	
Plywood floors	PVB	Laminated glass
	SBR	Installing plywood floors
Asphalt roofing	PUR	
	UF	Binders used in the manufacture of monomer
	SB	
	Acrylic	Glass mat for asphaltic shingle and roll roofing
Paper and film lamination	PVAC	Lamination of paper and vinyl film lamination to hardboard, plywood, and gypsum board for paneling
Thermal/sandwich panels	Epoxy	Interior, exterior partitions and cold-storage thermal-insulating panels
	Neoprene	
	PUR	
	Phenolic	
Mobile homes	PVAC	Gypsum board to wood joists
	PUR	
	Neoprene	
Modular homes	PUR	plywood to floor joists, gypsum board to studs, insulation board to exterior studs
	SBR	
Cellulose insulation	PVAC	Binding fibers and bonding fibers to the substrate
Parquet floors	SBR	Installation
Decorative brick	Acrylic	Installation
	SBR	Installation
Cove base	Acrylic	Installation
	SBR	Installation
Slate tiles	SBR	Installation
Asphalt tiles	Asphalt	Installation
	SBR	

**Table 17. Adhesives for Forest Products.**

<i>Application</i>	<i>Adhesive</i>	<i>Function/End Use</i>
Plywood	PF	Manufacture
	UF	Manufacture
	PUR	Patching
Particleboard	UF	Manufacture
	PF	
	MDI	
Oriented strandboard	PF	Manufacture
	MDI	
Medium-density fiberboard	UF	Manufacture
Waferboard	PF	Manufacture
Hardboard	PF	Manufacture
	UF	
Lumber laminating	RPF	
	MUF	

## Appliances

Adhesives are present in various large appliances with the bulk of the volume going into

refrigerators and freezers. Thermal and sound insulating materials are attached with adhesives in washers, driers, dishwashers, ranges, and air conditioners; cabinet sealing is another major application (Table 22).

## Packaging

One of the visible signs of an affluent society is the degree of packaging of consumer goods. In a few countries, e.g., the U.S., most products are wrapped. As packaging becomes more sophisticated, utilizing coated stocks and high speed equipment, the adhesive industry has had to develop products which adhere to a variety of substrates while meeting machine conditions.

The packaging industry is one of the largest outlets for adhesives. About 30 types of adhesives are employed in 35 different applications. Segments consuming large quantities of adhesives include corrugated board, case and carton sealing, bags, and tubes and cores (Table 23).

**Table 18. Furniture Adhesives.**

<i>Application</i>	<i>Adhesive</i>	<i>Function/End Use</i>
High pressure lamination	Neoprene	Lamination
	Polyamide	
	PVAC	
	UF	
Film overlay	PVAC	Lamination
	PUR	
	Epoxy	
	EVA	
	Neoprene	
	UF	
General assembly	PVAC	
	EVA	
	Animal glue	
Cabinets, counters	EVA	
	Epoxy	
Edge gluing	PVAC	Bonding strips of lumber stock to make core stock
	UF	
	EVA	
Edge banding	EVA	Attaching strips of veneer or vinyl around narrow edges of desks, tables, etc.
	PVAC	
	UF	
Wood veneer	PVAC	Attaching wood veneer to inexpensive substrates
	UF	

**Table 19. Automotive Adhesives.**

<i>Application</i>	<i>Adhesive</i>	<i>Function/End Use</i>
Auto-body		
Exterior	PVC plastisol SBR Epoxy PUR Silicone	Hood and deck lids, door-crash bars FRP bonding, hem flange bonding
Interior	SBS Polyester EVA Polyamide PUR SBR Acrylic	Carpet, package trays, vacuum-formed parts, headliners, fabric-foam seats
Under the hood	Anaerobic Halogenated elastomer Silicone Epoxy Polyester	Rubber bonding, formed-in-place gaskets, ra- diator components
Windshields	PVB film	Safety glass
Tire adhesives	Resorcinol-formalde- hyde Natural rubber	

**Table 20. Aircraft Adhesives.**

<i>Application</i>	<i>Adhesive</i>	<i>Function/End Use</i>
Structural films	Epoxy-nitrile Novolac epoxy Epoxy-nylon Nitrile-pheno- lic	Metal-metal bonding, honeycomb structures, composite bonding
Structural liquid	Epoxy	Assembly
Nonstructural liquid	Neoprene Nitrile	Interior assembly
Safety glass	PVB film	Laminated glass

**Table 21. Electrical/Electronic Adhesives.**

<i>Application</i>	<i>Adhesive</i>	<i>Function/End Use</i>
Batteries	Epoxy PP	Bonding tops and bottoms of battery cases made of rubber
TV tubes	Epoxy Polyester	Implosion proofing
Built-up mica	Silicone Epoxy Shellac Polyester	
Magnet bonding	Acrylics Epoxy Cyanoacrylate	Mixers, audio speakers
Flexible printed circuits	Acrylic Polyester Epoxy	Lamination of foil-film
Conductive	Epoxy	Die attachment

**Table 22. Appliance Adhesives.**

<i>Application</i>	<i>Adhesive</i>	<i>Function/End Use</i>
Refrigerators and freezers	PP Polybutene Epoxy EVA	Seal, cabinets, seal holes made for refrigeration liners
Washers and dryers	SBR Cyanoacrylate Anaerobic	Attaching insulating materials Assembling of plastic components of control panels Threadlocking
Air conditioners	SBR Silicone	Attaching insulating material Bonding aluminum tubes
Dishwashers	SBR Silicone	Attaching insulating material Bonding plumbing fixtures
Microwave ovens	Silicone	Assembly of viewing windows
Ranges	SBR Silicone	Attaching insulating material Assembly of viewing windows

**Table 23. Packaging Adhesives.**

<i>Application</i>	<i>Adhesive</i>	<i>Function/End Use</i>
Corrugated board	Starch	Fabrication
Solid fiberboard	PVOH	Lamination
Can assembly	PVAC EVA	
Case sealing	EVA PVAC Dextrin	
Folding carton	PVAC EVA PE	Assembly, sealing
Tray forming	EVA PE PVAC	
Setup boxes	Animal glue PVAC	
Bags	PE PP PVAC Starch Natural rubber EVA	Heavy duty Heavy duty Heavy duty, mailer Heavy duty, grocery Heavy duty Mailer
Gummed Tape/Paper	Starch Dextrin Animal glue PP PVAC SBR	
Envelopes	Dextrin PVAC Natural rubber Animal glue	Front seal, back gum, window patch Front seal, back gum, window patch Front seal Front seal

(Continued on page 34)

**Table 23. (Continued)**

<i>Application</i>	<i>Adhesive</i>	<i>Function/End Use</i>
Paperboard lamination	PVOH PVAC Dextrin	
Cap liner	PVAC PUR	
Reinforced web	PP Asphalt PVAC	
Lamination	PUR  Acrylic PVAC Butyl Nitrile Neoprene Silicate	Film-film, film-foil, film-paper, foil-paper Film-film, film-paper, foil-paper Film-film, film-paper Film-film Film-film Foil-paper Foil-paper
Paper tubes and cores	Silicate PVOH Starch PVAC	
Composite cans	PVAC PVA Dextrin Silicate EVA PE Polyamide	
Fiber drums	Silicate PVOH EVA	
Labeling	Casein Dextrin EVA PVAC S-B-S Rosin Starch	Glass Glass, plastic, corrugated Glass, plastic, can Plastic, can, corrugated Plastic Can Can
Paper cups and tubs	PVAC Starch	
Cigarette making	PVAC Starch EVA	
Metal can sealing	SBR Neoprene	

## Bookbinding

Were it not for adhesives, this Handbook could not be assembled. About one-half of the adhesive volume in bookbinding goes for binding edition books (hardcover); the balance is dis-

tributed among several types of publications including softcover books, magazines, directories, and catalogues.

“Perfect binding” is a method that has penetrated every type of publication. In this operation, the sewing of signatures is eliminated,

and the assembling of book sections—trimming the back, applying hot melt adhesive, fastening the cover, and trimming the remaining sides of the books— requires less than 10 seconds (Table 24).

### Pressure Sensitives

Pressure sensitive masscoats are applied to backings such as paper, polyester film, PVC,

acetate, polypropylene, polyethylene, foam, cloth, etc., in order to make tapes, labels and decals.

The adhesives are elastomeric. In 1975, almost two-thirds of the adhesives were solvent-based; a dozen years later, their share had declined to about one-third. Besides solvent systems, pressure-sensitive adhesives can be 100% solids, emulsions, and radiation-curable (Table 25).

**Table 24. Bookbinding Adhesives.**

<i>Application</i>	<i>Adhesive</i>	<i>Function/End Use</i>
Edition Books		
Casemaking	Animal glue	Making the cover
Casing-in	PVAC	Mounting the book in the case by binding end sheets of the outside pages to the cover
“Perfect bound”	EVA Styrenic block co-polymers	
Gluing-off	PVAC	Adhesive placed over signatures
Lining	EVA Animal glue	Crash (scrim fabric) is glued to signatures; kraft paper is bonded to crash
Softcover Books	EVA	Perfect binding
Magazines	EVA S-B-S	Perfect binding
Directories	Animal glue EVA	Perfect binding
Catalogues	EVA Animal glue	Perfect binding
Business Forms	PVAC Dextrin EVA	

**Table 25. Pressure-Sensitive Adhesives.**

<i>Applications</i>	<i>Adhesives</i>	<i>Function/End Use</i>
Tapes	Natural rubber Butyl Styrenic block copolymer SBR Acrylic Silicone	Retail, commercial, packaging, electrical duct pipe wrap, medical, other
Labels and decals	Styrenic block copolymers SBR Acrylic SBR PIB	Paper Permanent, removable, freezer; plastic labels and decals

### Textile

Adhesives are employed in many textile applications. In tufted carpeting, they have become an integral part of the operation. They provide added strength and stability to nonwovens and fiberfill. Flocking adhesives enable fabrics to look like suede (Table 26).

### Assembly of Disposables

Several types of adhesives, mainly hot melts, are employed in the construction of diapers, sanitary, medical, and surgical products. In the past, this application was solidly held by polyolefin hot melts. However, styrenic block copolymers are rapidly penetrating this market. They are elastomeric, thus have the advantage of stretchability. The principal bonding operation is adhering the nonwoven absorptive web

to the polyethylene moistureproof shield (Table 27).

### Consumer Adhesives

Over a dozen types of adhesives are useful around the home, office, and shop. The applications are diverse. "White glue" continues to be the indispensable staple for bonding paper, wood, etc. Epoxy and cyanoacrylates are the "miracle glues" able to bond more difficult substrates (Table 28).

### Shoes

About 80% of the shoes sold in the US are now imported; but domestic shoe production continues to demand an impressive array of adhesives. These materials are needed to make various shoe components and to attach the

**Table 26. Textile Adhesives.**

<i>Application</i>	<i>Adhesive</i>	<i>Function/End Use</i>
Carpeting	C-SB VDC/SB PUR PVC EVA PE PVAC	Residential, contract, automotive
Nonwoven	Acrylic PVAC C-SB PVC	Diapers, sanitary, medical, wipes, towels, apparel, other
Fiberfill and shoddy pad	PVAC Acrylic PVC C-SB	Furniture, home furnishings, filter, automotive, carpet, other
Flocking	Acrylic	Home furnishings, apparel, other
Tie coats	PUR Acrylic PVC	Footwear, handbags, apparel, upholstery, automotive, other
Laminating	PVC Acrylic	Apparel Automotive tarpaulins, other
Fusible interlinings	PA PE Polyester PVC	Apparel
Labels and emblems	Polyester PA PUR PVC	

**Table 27. Disposable Assembly Adhesives.**

<i>Application</i>	<i>Adhesive</i>	<i>Function/End Use</i>
Assembly components	EVA	Diapers, sanitary, medical, surgical
	Styrenic block copolymers	
	PE	
	PP	
	PVAC	

**Table 28. Consumer Adhesives.**

<i>Application</i>	<i>Adhesive</i>
White glue	PVAC
Contact cement	Neoprene
Rubber cement	Natural rubber
Household cement	Cellulose nitrate
	Cyanoacrylate
	Epoxy
Glue stick	Wax
Hot melts	EVA
Library paste	Starch
	Dextrin
	Starch
	Animal glue
	Silicone
Mucilage	Anaerobic

soles, either permanently (cemented shoes) or temporarily (preparatory to stitching). High performance polyester and polyamide hot melts have achieved acceptance for many operations (Table 29).

### Abrasives

Abrasives are hard, inert particles such as silicon carbide and aluminum oxide used for cutting, shaping, polishing, or cleaning. The adhesive functions as a binder in the manufacture of bonded and coated abrasives. A bonded abrasive such as a grinding wheel is a molded mixture of abrasive particles and binders. In a coated abrasive, e.g., sandpaper or emery paper, a particle layer is glued to a flexible backing. The predominant binder is phenolic resin (Table 30).

### Friction Materials

Friction materials have been made mainly from asbestos or other fiber and an organic binder. These materials are used as brakes and clutches

**Table 29. Shoe Adhesives.**

<i>Adhesive</i>	<i>Function/End Use</i>
PUR	Sole attaching
Neoprene	Sole attaching
Natural rubber	Sole attaching, combining box toe, doubling and box
Polyamide	Lasting, toe, folding, heel attaching
Polyester	Lasting
EVA	Box toe, shank attaching

**Table 30. Binders for Abrasive Materials.**

<i>Application</i>	<i>Adhesive</i>	<i>Function/End Use</i>
Coated abrasives	Phenolics	Sand paper
	Animal glue	
	UF	
Bonded abrasives	Phenolics	Grinding wheel
	Epoxy	
	Alkyd	
	Natural rubber	
	SBR	
	Shellac	
	Polyimide	

in automobiles and construction equipment, brakes in elevators and automatic washing machines, etc. Phenolic and modified phenolic resins are the principal binders, followed by oleoresinous and rubber (nitrile and natural), which generally have lower heat resistance and are found mainly in products for the automotive aftermarket.

Because asbestos is carcinogenic, various non-asbestos substitutes have been introduced: glass fiber, aramid fiber (Kevlar), carbon fiber, etc. A common combination is glass fiber/phenolic (Table 31).

### Foundry Sand Binders

Another outlet for binders is to hold together the sand in the fabrication of castings. Iron and



**Table 31. Friction Material Binders.**

<i>Adhesive</i>	<i>Function/End Use</i>
Phenolic	Brakes, clutches
Rubber	
Oleoresinous	

**Table 32. Foundry Sand Binders.**

<i>Adhesive</i>
Phenolic
Alkyd-isocyanate
Furan siliceous
Oil-based

steel castings have been declining while non-ferrous castings, mainly aluminum base, are gaining. The automotive industry is the major user of castings. Phenolic resins are the most common type of binder utilized (Table 32).

**KEY TO ADHESIVES**

ABS	acrylonitrile-butadiene-styrene
CPVC	chlorinated polyvinyl chloride
C-SB	carboxylated styrene-butadiene
EVA	ethylene-vinyl acetate
MDI	methylene-diphenylene isocyanate
MUF	melamine-urea-formaldehyde
PE	polyethylene
PF	phenol-formaldehyde
PP	polypropylene
PUR	polyurethane
PVAC	polyvinyl acetate
PVB	polyvinyl butyral
PVC	polyvinyl chloride
PVDC	polyvinylidene chloride
PVOH	polyvinyl alcohol
RPF	resorcinol-phenol-formaldehyde
SBR	styrene-butadiene rubber
SBS	styrene-butadiene block copolymer
SIS	styrene-isoprene block copolymer
UF	urea-formaldehyde

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# Fundamentals of Adhesion

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## INTRODUCTION

Adhesion is the interaction that develops between two dissimilar bodies when they are contacted. Adhesion is thus a multidisciplinary science dealing with the chemistry and physics of surfaces and interfaces as well as the mechanics of deformation and fracture of adhesive joints. In this overview, these various aspects of adhesion are discussed. We begin by describing the general types of adhesive bonds. This is followed by sections on solid surfaces and their characterization, interfacial properties, surface treatment, and finally a discussion of the mechanics of adhesive joints.

## Bond Types

**Immiscible Planar Substrates.** Consider the simplest case in which a liquid adhesive is placed on a molecularly smooth solid substrate with which it is totally immiscible. The time-dependent process whereby the adhesive and substrate come into intimate contact is called *wetting*. The *interface* is a plane across which molecular forces of attraction, also denoted *intrinsic adhesion*, exist between the liquid and solid. These forces range in magnitude from strong covalent or ionic chemical bonds to weaker physical adsorption, e.g., H-bonding, dipole-dipole, and van der Waals interactions.

One method which has been used to characterize interfacial forces is based on specific donor-acceptor (acid-base) interactions between adhesive and substrate molecules.<sup>1</sup> Here, functional groups in each material are assigned an acid or base strength, which then can be used to calculate expected bond strengths. Further discussion of this approach is delayed to a later section.

In some instances, it has been proposed that intrinsic adhesion is due to electrostatic forces developed between materials with different electronic band structures.<sup>2-4</sup> These forces are attributed to transfer of electrons across the interface, creating positive and negative surface charges that attract one another. There is serious disagreement about the magnitude of electrostatic attractions compared to other physical forces. One author<sup>5</sup> concludes that electrostatics make a negligible contribution to adhesion; others<sup>6,7</sup> maintain that these forces are dominant.

**Immiscible Substrates with Complex Surface Topography.** As before, the substrate is assumed to be completely immiscible with the adhesive, so that adhesive-substrate interactions are limited to surface sites. However, the substrate surface topography is now complex, as depicted schematically in Fig. 1. Be-

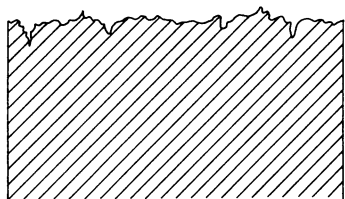


Fig. 1. Micro-rough solid surface.

cause of pores, depressions, and asperities, there are many more surface sites available to interact with an adhesive compared to a planar substrate. Thus, if the adhesive has sufficient mobility and the wetting forces are high enough, the extent of intrinsic adhesion may be increased by surface roughening. On the other hand, poorly wetting, viscous adhesives may form relatively few interactions with roughened substrates, especially if the (wetting) time from adhesive application to solidification (setting) is short.

Another consequence of the topography shown in Fig. 1 is mechanical interlocking between the adhesive and substrate. This is dependent on the specific shape of the interface. Good joint strengths can be obtained because of this even when the intrinsic interaction is low. Mechanical interlocking plays an important role in bonding wood, textiles, or paper because of their finely divided and porous nature. In addition, many metals and plastics are etched before bonding, so that the adhesive can penetrate and lock into them. When mechanical interlocking is substantial, the region around the interface forms a composite interlayer that can be viewed as an entity coupling the two bulk materials.

#### Partially or Fully Miscible Substrates.

When the adhering materials are partially or fully miscible with one another, there will be formed between them an *interphase* consisting of interdiffused molecules from each material.<sup>8</sup> The thickness of this interlayer depends on the thermodynamic compatibility of the materials as well as molecular diffusion rates. Molecular interdiffusion is quite different from mechanical interlocking. The former involves interpenetration at the molecular level, whereas in the latter case, the bulk adhesive flows into and

around surface features of the substrate that are much larger than molecules.

Interdiffusion is important when bonding two polymers together; if there is a strong affinity between the different types of molecules, then the interphase will be relatively thick and the extent of intrinsic adhesion high.

In some cases, the contacted materials not only interdiffuse but also chemically react with one another. Here, the interphase is not just a "physical blend," but becomes a new chemical entity.

#### Immiscible Substrates with Interphase Formation via Chemical Reaction.

This is a rather special case, but is technologically important. Here, although the contacting materials are not miscible, each contains a component which can diffuse to the interface and chemically react, thereby forming in situ a new interphase which couples the two materials together.

When rubber containing sulfur and curatives is pressed into contact with brass (typical alloy ~70% copper, 30% zinc) and then vulcanized, copper ions diffuse to the brass surface where they combine with sulfur to form a cuprous sulfide interphase.<sup>9</sup> Joint strengths are controlled by the characteristics of this layer. This bonding is of critical importance in tires reinforced with brass-plated steel cords, and has been extensively studied.<sup>10-12</sup>

#### Setting

After an adhesive wets a solid substrate, it is normally necessary to convert it to a hardened state (setting) so that the joint will be capable of supporting stresses. Setting of adhesives can occur by physical or chemical means. In order to minimize internal stresses in a joint, there should not be a large change in volume of the adhesive during solidification, and the thermal expansion coefficients of the adhesive and adherends should be similar. This is especially important when the solid adhesive has a high modulus. Furthermore, joints with plane interfaces have been suggested<sup>13</sup> to be more sensitive to adhesive shrinkage than are joints made with complex, high surface area adherends. Solvent-based adhesives experience the most

shrinkage during setting compared to those which harden by cooling (hot melt) or by chemical reaction (usually thermosets). The fact that epoxy resins shrink only about 3% upon setting is one reason for their good performance. Another advantage of epoxy solidification reactions compared to many other condensation polymerizations is that no small molecules, e.g., water, which can interfere with bonding, are created during setting. Polyurethane reactions are also favorable in this regard.

Some inorganic substances adhere exceptionally well because they expand upon freezing. For example, ice will adhere to almost any surface, even those not wetted well by water.<sup>14</sup> When water freezes in a depression in a solid surface, expansion causes it to lock against the sides of the depression and form a strong joint. Attempts<sup>15,16</sup> have been made to develop organic adhesives, based on ring opening polymerizations, that expand upon setting.

### Adhesive Joint Strengths

An adhesive joint consists of two or more adherends held together by adhesion. The strength is assessed by loading it until fracture. Commonly determined<sup>17-20</sup> are the average fracture stress and the fracture energy—neither of which is readily related to intrinsic adhesion, even if the locus of failure is fully interfacial. One reason is the uncertain contribution to strength from mechanical interlocking. There is, however, another reason, even when mechanical interlocking is absent. During fracture of an adhesive joint, the adhesive and bonded members are deformed by the applied forces. All materials are imperfectly elastic to some degree, i.e., they do not return all the energy expended in deforming them. In general, during fracture, not only is energy expended in cleaving bonds to create new free surface, but also energy is expended away from the interface within the bulk of the bonded members. This causes the fracture energy from a mechanical test to exceed intrinsic adhesion, which depends only on the number and types of bonds disrupted at the interface. Thus, to judge intrinsic adhesion by a measured mechanical strength may be misleading. For example, if an adhesive is modi-

fied by adding fillers or tackifiers, and the modified adhesive gives a higher joint strength than the unmodified one, it is tempting to conclude that the intrinsic strength of adhesion has been enhanced. But the bulk properties of the adhesive are also modified by the addition of filler and the improved performance may merely reflect a higher dissipation of mechanical energy within the adhesive layer. To understand the performance of an adhesive bond it is therefore essential to recognize the role of the bulk properties of the bonded members, as well as interfacial energetics, in determining the bond strength.

Fracture analyses and the role of energy dissipation are addressed later after considering surface properties.

## SURFACES AND THEIR CHARACTERIZATION

### Solids

With few exceptions (such as carefully cleaved mica), all solid surfaces are rough at dimensions of a few Ångströms. They contain asperities, pores, depressions, projections, etc. of one sort or another, depending on their nature and the way in which the solid was processed. For example, the average roughness of a machined metal is about 3–6  $\mu\text{m}$ . Even after polishing, surface irregularities in the range of 0.02–0.25  $\mu\text{m}$  remain.<sup>14</sup> At a smaller scale, the oxide on a metal may have a complex high-surface-area structure, which, at an even smaller scale, may itself contain non-uniformities like growth steps and depressions at grain boundaries.

**Surface Oxides and Contaminants.** All metal surfaces that have been exposed to the atmosphere have an oxide layer on them.<sup>21</sup> Iron can have various types of oxide:  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ , and  $\text{FeO}$ . With copper, the oxide layer closest to the base metal is  $\text{Cu}_2\text{O}$ , while the outermost layer is  $\text{CuO}$ . Alloys such as stainless steel and brass have mixed oxide layers of each component metal. The thickness of the oxide layer depends on the nature of the metal and the environment. Some metals, e.g., aluminum and titanium, form thin, tough, tenaciously adher-

ing oxides, which passivate the surface and prevent continued oxidation. Others, like iron, have oxides which continue to grow, especially in a humid environment. Formation of oxide on a metal is thought to involve first chemisorption of oxygen on the surface, followed by chemical reaction to form the oxide. The distinction between chemisorption and chemical reaction is the retention of chemical identity of the interacting species, which may be recovered intact by supplying desorption energy in the case of chemisorption, while this is not generally possible in the case of chemical reaction.

In practice, metal oxides are covered with organic molecules and water adsorbed from the atmosphere.<sup>22</sup> Other common sources of surface contamination are residual processing oils and lubricants. Whether the interacting species are considered physically adsorbed or chemisorbed depends on the strength of interaction. Although somewhat arbitrary, it has been stated<sup>23</sup> that interactions up to 10 kcal/mole are considered physical adsorption, while those greater than 10 kcal/mole are regarded as chemisorption.

Another source of surface contaminants is from the bulk.<sup>21</sup> For example, iron containing only 10 parts per million of carbon has been shown to form a carbon-rich structure on its surface upon heating or straining. In addition to carbon, other species, including sulfur, nitrogen, boron, and oxygen have been shown to diffuse from the interior of metals to their surfaces. A recent paper<sup>24</sup> discusses several methods to characterize metal surfaces.

It is also common for some polymeric compounds to form surface regions with compositions different from the bulk material, by selective diffusion of components. This process is termed *blooming* when the surface layer is solid, and *bleeding* if the surface is liquid. Sulfur and fatty acid blooms can inhibit adhesion in rubber laminates.<sup>25</sup> Gillberg<sup>26</sup> has published an overview on polymer surface analysis.

### Characterization of Surface Topography.

**Profilometry.** One common method to study surface geometry is with an electromechanical profilometer.<sup>27</sup> Here a diamond stylus passes across the surface at constant speed and follows

its contour. The magnitude of surface irregularities are amplified and plotted, giving the surface profile. It is possible to profile a solid surface in several directions and generate a surface topographical map.<sup>28</sup> Although useful, profilometry has inherent limitations owing to the finite size of the stylus. Thus, it is very difficult to follow the true surface profile for sharply varying surfaces. Additionally, surface profiling cannot give information about surface roughness at dimensions below about 0.1  $\mu\text{m}$ .

**Microscopy.** The best methods to determine detailed surface topographies are by optical and scanning electron microscopy. The optical microscope is limited by a lack of depth of focus and a resolution limit of about 2000 Å, but these limitations are overcome in the scanning electron microscope (SEM). The depth of focus is up to 300 times that of the optical microscope and the resolution limit is only a few Ångströms.<sup>29</sup>

**Structural and Chemical Analysis.** *Low Energy Electron Diffraction (LEED).* In this technique,<sup>30</sup> a low energy electron beam (<200 eV) is directed at the surface of a crystalline solid, which serves as a diffraction grating. Electrons only penetrate the first few atomic layers and some of them are diffracted back onto a fluorescent screen, giving a distinctive pattern characteristic of the structural arrangement of atoms in the outermost atomic layers. LEED is most effective for examining the surface structure of a single crystal or polycrystalline sample made up of large grains so that the primary electron beam can be directed at a small region within one grain or another.

In one case,<sup>31</sup> this method was used not only to elucidate contaminants on an iron surface, but also to reveal surface strain produced when the iron surface was bombarded with an argon ion beam to remove the contaminants.

**Attenuated Total Reflectance Spectroscopy (ATR).** ATR, also called internal reflection spectroscopy, is a technique used to characterize the surface region of a polymeric composition.<sup>32</sup> A sample is placed on both sides of an appropriate crystal and an infrared beam within the crystal is repeatedly attenuated as it is reflected back and forth from one sample surface to the other. The intensity of the attenuated

beam is monitored for a range of wavelengths. Since ATR has a sampling depth of about 0.3–3.0  $\mu\text{m}$ , it is not well suited for characterizing surface composition on a molecular scale. However, it is useful for studying migration or diffusion of compounding ingredients in the surface region of a polymer sample.<sup>33,34</sup> For example, ATR analysis has shown<sup>35</sup> that a pressure sensitive adhesive made up of natural rubber and a wood rosin tackifying resin has a surface region richer in tackifier than the bulk adhesive.

**Electron Microprobe.** A common attachment to the SEM is the electron microprobe.<sup>36</sup> With this tool, an electron beam is focused at a sample surface, causing ionization to a depth of a few micrometers. Energies and wavelengths of the x-rays emitted during de-excitation are characteristic of the elements present in the solid. Measured intensities of the x-rays can be compared with intensities of x-rays from a pure standard of a given element, to yield an estimate of the amount of that element in the sample. While the electron microprobe does not give a strictly surface analysis, it does have the desirable capability of determining a “spot by spot” analysis of surface regions.

An advantage of the SEM–electron microprobe combination is the opportunity to examine the topography of the surface of a sample by SEM, and then to focus on a small feature of interest, e.g., a particle on a fracture surface, and use the electron microprobe to identify the composition at that specific location.

**Auger Electron Spectroscopy (AES).** When the surface of a solid is bombarded with electrons, causing ionization, one way for energy to be conserved during de-excitation is by emission of electromagnetic radiation (x-rays). This is the basis of the previously described technique. Alternatively, some of the energy released by de-excitation is carried away by emission of a secondary (Auger) electron, whose detection is the basis of AES.<sup>37</sup> The emission is a two-step process: an excited electron drops into a core vacancy and an Auger electron escapes. The energy of an Auger electron depends on the chemical bonding state of the element from which it escaped. Unlike x-rays, the maximum depth from which Auger electrons can escape is only about 0.3–0.6 nm

for many materials; metals have the shortest escape depths, whereas insulators have the greatest. Thus, Auger spectroscopy is a technique that truly characterizes the surface of the irradiated specimen. Lateral resolution is of the order of 1  $\mu\text{m}$ .

AES uses a low energy, 1–5 keV, electron beam gun to minimize surface heating, which could desorb some materials from the surface or cause decomposition of adsorbed organics. To enhance the signal, a low angle of incidence is used, which increases the extent of interaction with surface atoms. The energy and number of the emitted Auger electrons are detected by an energy analyzer and counter. The energy identifies the element from which the electron came and the number is a measure of its abundance.

**Electron Spectroscopy for Chemical Analysis (ESCA) or X-ray Photoelectron Spectroscopy (XPS).** In XPS, the surface is bombarded with low energy x-rays, resulting in ionization by direct ejection of a core-level electron (a photoelectron).<sup>38,39</sup> The number and energies of photoelectrons are monitored. The following simple relationship holds:

Binding of photoelectron

$$= \text{Incident x-ray energy} - \text{Kinetic energy of emitted photoelectron} + \text{Spectrometer work function} \quad (1)$$

The last term on the right-hand side can be determined during spectrometer calibration and is typically about 5 eV. The binding energy of a photoelectron is characteristic of the element from which it came and the way in which that element is chemically bonded. Atoms bound to more electronegative species emit photoelectrons with higher binding energies. Only hydrogen and helium are difficult to detect because their x-ray absorption cross sections are very small. The maximum sensitivity for most elements with XPS is approximately 0.01 atomic layer; the sampling depth is typically in the range of 15–50 Å. Although XPS is less sensitive than AES, it gives simpler line shapes and provides a direct measure of binding energies.

XPS has been used to characterize polymers that have been surface treated prior to adhesive bonding.<sup>40</sup> It has also been employed to study surface contamination<sup>22</sup> and to identify the locus of failure in adhesive joints.<sup>41-48</sup>

In a study of aluminum-epoxy adhesive joints, Dillingham and Boerio<sup>42</sup> used XPS analysis to determine that, after humid aging, the locus of fracture was within the metal oxide. They further proposed that catalysis during setting by acidic hydroxyls on the oxide caused the epoxy near the oxide to be more crosslinked than the bulk epoxy network. Another researcher<sup>48</sup> showed that fracture progressed within a weak boundary layer when a polyvinylidene fluoride-nylon bond was ruptured.

XPS and AES instruments are often equipped with an argon ion gun. Ion impingement to sputter away material, and surface analysis, can be alternated to give a composition depth profile.

*Ion-Scattering Spectroscopy (ISS).* ISS utilizes low energy (0.1–3 KeV) inert gas ions as the incident beam.<sup>49</sup> A fraction of these ions undergo collisions with surface atoms and are backscattered with some loss of energy. Back-scattering will only occur from atoms at the surface, since ion neutralization occurs for incident ions that penetrate beyond the first layer.

If the incident ions have energy  $E_0$  and mass  $M_i$ , then the ions which scatter from a surface atom of mass  $M_s$  will have a rebound energy  $E$ :

$$E = \frac{E_0}{(1 + X)^2} \cdot [\cos \theta + (X^2 - \sin^2 \theta)^{1/2}]^2 \quad (2)$$

where  $\theta$  is the scattering angle and  $X = M_s/M_i$ . An ISS spectrum consists of the energy distribution of ions rebounding from a sample, with peaks occurring at specific values of  $E$ . Equation (2) can be used to calculate the masses of the surface atoms.

A feature of ISS is that the surface is being continuously sputtered away during measurement, so that the spectra may change if there is a composition gradient beneath the surface. Another feature of the method is that it can be used to obtain elemental analysis at concentra-

tions as low as  $10^{-3}$  to  $10^{-4}$  monolayer coverage.

*Secondary Ion Mass Spectroscopy (SIMS).* The incident beam for SIMS is the same as that for ISS, but secondary ions from the target are monitored, rather than the back-scattered primary-beam ions.<sup>50,51</sup> These secondary ions are mass analyzed to give an indication of surface composition. Like ISS, it is very sensitive—able to detect parts per million quantities of certain elements. Additionally, hydrogen can be detected, and, in some cases, chemical structure can be determined more directly than with XPS or AES. The sampling depth for SIMS is two to four atomic layers.

The spectra consist of plots of the intensity of secondary ions against  $E/E_0$ . One problem with the general application of SIMS is that secondary ion yields may vary by several orders of magnitude for different elements and for the same element in different matrices. This often makes quantitative analysis difficult without suitable standards. SIMS is most commonly used for inorganic surfaces, although Briggs<sup>52</sup> has discussed its application to polymers.

## Liquids

Consider a liquid which is in contact with ambient air. A molecule in the surface does not interact with other liquid molecules in the same way as do liquid molecules in the interior. It experiences instead a different, much weaker interaction, at the air interface.<sup>53</sup> Thus, surface molecules experience a net attraction toward the interior and have an energy exceeding that of bulk molecules. A drop of liquid in the absence of any external forces will spontaneously take a spherical shape, thereby minimizing surface area and free energy. It behaves as though it were covered with an elastic skin, resisting shape changes that would necessitate the movement of molecules from the bulk to the surface. At constant temperature and pressure, the increase in Gibbs free energy accompanying a unit area increase in surface area of a liquid is, by definition, the surface tension  $\gamma$ . Alternatively,  $\gamma$  may be viewed as the force per unit length tending to contract the surface and cause a liquid to resist spreading.

## INTERFACES

We turn now to the interaction that develops when a liquid is placed on a solid. In order for two substances to interact directly, the molecules of one must come within a few Ångströms of those of the other, i.e., the liquid must adsorb onto the solid surface. This is an exothermic process as can be readily shown from a simple thermodynamic argument. The free energy of adsorption,  $\Delta G_{AD}$ , is given by the well known equation

$$\Delta G_{AD} = \Delta H_{AD} - T\Delta S_{AD} \quad (3)$$

where  $\Delta H_{AD}$  and  $\Delta S_{AD}$  are the enthalpy and entropy change upon adsorption. If adsorption is to take place spontaneously,  $\Delta G_{AD}$  must be negative. Moreover, since adsorption of a liquid restricts the freedom of the liquid,  $\Delta S_{AD}$  is always negative. Consequently,  $\Delta H_{AD}$  must be negative.

Figure 2 shows a small portion of the interfacial region as a liquid (adhesive) is brought into contact with a solid substrate. Certain factors hinder bond formation, whereas others promote it. Barriers include: (1) surface rugosity, (2) species adsorbed on the solid before bonding, (3) air entrapped in micropockets between the liquid and solid, (4) surface tension of the liquid and its bulk viscosity arising from cohesive forces among liquid molecules. Fac-

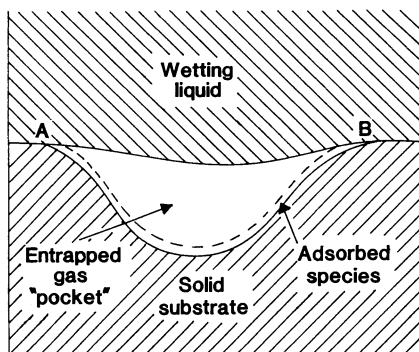


Fig. 2. Portion of solid surface soon after contacting with a viscous liquid. Some wetting has taken place, but a pocket of gas has been trapped in a depression. Molecular attraction between liquid and solid at the periphery (locations A and B) of the micro-bubble tend to increase the true contact area.

tors to promote bonding are: (1) any applied pressure and (2) intrinsic attractive forces between liquid and solid. In principle, it is desirable for the liquid to possess moieties with strong molecular attraction for the substrate without, at the same time, giving rise to strong molecular interactions among liquid molecules themselves. For example, a liquid molecule capable of H-bonding with a substrate, but not with like liquid molecules, would be expected to wet a substrate well. Ester linkages cannot form hydrogen bonds with each other but are, in principle, capable of hydrogen bonding to surface silanol groups on glass.

The hindrance to wetting imposed by surface impurities must also be considered. Wetting is promoted if adsorbed and entrapped gases are readily solubilized into the adhesive. Consider the microbubble depicted in Fig. 2, containing entrapped air. At the periphery of the bubble, forces between the adhesive and substrate tend to increase progressively the area of true interfacial contact. As the microbubble is reduced in size, the pressure within the bubble will increase unless the gas is adsorbed at a sufficiently rapid rate into the adhesive mass. If there is a pressure increase within the bubble, this would slow the wetting process—in essence, the wetting forces are resisted by the pressure tending to reopen the interface. Whether or not this process is important in influencing the kinetics of wetting will depend on the rate at which entrapped impurities are adsorbed into the adhesive.

It is known that many polar substrates such as glass or metals, which have been exposed to ambient air, have several molecular layers of adsorbed moisture on them. Thus, features within the adhesive that solubilize surface moisture may be important in speeding up wetting. Perhaps this is one role of polar groups in a typical adhesive. Certainly an adhesive that is completely incapable of displacing or solubilizing surface moisture would find it difficult, if not impossible, to attain rapid molecular contact with the actual substrate.

## Thermodynamics of Adhesion

**Contact Angle.** The previous discussion of bond formation (wetting) was qualitative in na-



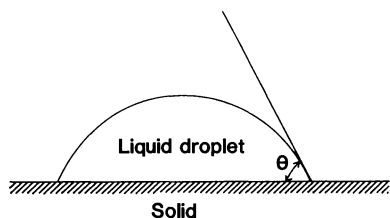


Fig. 3. Contact angle of a liquid droplet on a planar solid surface.

ture. Application of thermodynamic principles to wetting and adhesion is one way to quantify these phenomena.<sup>54,55</sup> The extent to which a liquid wets a solid is measured by the contact angle,  $\theta$ . Fig. 3 depicts a liquid droplet on a planar solid surface. When  $\theta$  is large, the liquid tends to minimize its area of contact (interaction) with the solid; this indicates a preference of liquid molecules to interact among one another rather than with the solid. On the other hand, when  $\theta = 0$ , the liquid spreads freely over the surface and is said to completely wet it. This occurs when the molecular attraction between the liquid and solid is greater than that between similar liquid molecules.<sup>56</sup> As a result, liquid-liquid interactions are disrupted in favor of creating new liquid-solid interactions. Stated alternatively, a contact angle of zero is a condition where the number of solid-liquid interactions is maximized.

For a liquid droplet on a solid in the presence of saturated vapor of the liquid, the relationship between contact angle and the surface tensions (or free energies) is given by Young's equation,<sup>57</sup>

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \quad (4)$$

where  $\gamma_{sv}$  = solid-vapor surface tension;  $\gamma_{sl}$  = solid-liquid surface tension; and  $\gamma_{lv}$  = liquid-vapor surface tension.

A widely used method for approximating the surface tension of a solid was developed using contact angle measurements.<sup>58</sup> A plot of  $\cos \theta$  against the surface tension  $\gamma$  for a homologous series of liquids can be extrapolated to give a critical surface tension of  $\gamma_c$  at which  $\cos \theta = 1$ ; two such plots are shown in Fig. 4.<sup>59</sup>

Any liquid with a surface tension less than  $\gamma_c$  completely wets the solid surface. The critical

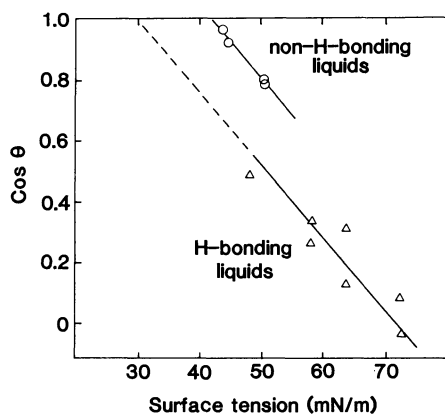


Fig. 4. Comparison of Zisman plots of H-bonding and non-H-bonding liquids on polystyrene. (Data taken from Ref. 59.)

surface tension  $\gamma_c$  has been taken as an approximate measure of the surface free energy  $\gamma_{sv}$  of a solid. The precise value of  $\gamma_c$  is dependent on the particular series of liquids used to determine it. A series of polar H-bonding liquids give a lower  $\gamma_c$  than simple hydrocarbons, which interact less strongly with the same surface.<sup>59</sup>

Polyolefins and fluorocarbon polymers have low values of  $\gamma_c$  and are said to have low energy surfaces; these materials are difficult to wet and bond. Metals, ceramics and polar polymers have high value of  $\gamma_c$  (high energy surfaces), can be readily wet by many organic adhesives, and exhibit good bondability.

Good proposed another expression that relates interfacial tension  $\gamma_{sl}$  to the individual surface tensions of a liquid and solid.<sup>60</sup>

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2\phi(\gamma_{sv}\gamma_{lv})^{1/2} \quad (5)$$

The last term represents the reduction in interfacial tension owing to molecular attraction between the liquid and solid. The term  $\phi$  is defined by:

$$\phi = \frac{W_a}{(W_{cl}W_{cs})^{1/2}} \quad (6)$$

where  $W_{cl}$  and  $W_{cs}$  are the work of cohesion of the liquid and solid, respectively, i.e., the thermodynamically reversible work required to create a unit area of new surface in each ma-

terial.  $W_a$  is the thermodynamic work of adhesion (see below). For simple interfaces,  $\phi$  is approximately unity, but for systems in which there are different types of intermolecular force in the two substances,  $\phi$  may be appreciably less than unity.

By combining Eqs. (4) and (5), an expression for  $\gamma_{sv}$  can be obtained:

$$\gamma_{sv} = \frac{\gamma_{lv}(1 + \cos \theta)^2}{4\phi^2} \quad (7)$$

From the preceding discussion, as  $\theta \rightarrow 0$ , then  $\gamma_{lv} \rightarrow \gamma_c$  (Zisman plot). Substituting this condition in Eq. (7), it is found that

$$\gamma_c = \phi^2 \gamma_s \quad (8)$$

Thus, the critical surface tension  $\gamma_c$  for wetting is predicted to be approximately equal to the surface tension or energy  $\gamma_{sv}$  of the solid only when  $\phi = 1$ , i.e., for simple interfaces for which  $W_a = (W_{cs}W_{cl})^{1/2}$ .

**Work of Adhesion.** If a liquid is placed on a solid surface with which it has no interaction whatsoever,  $\theta = 180^\circ$  and Eq. (4) simplifies to

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} \quad (9)$$

That is, the interfacial tension is simply the sum of surface tensions of the liquid and the solid. However, in all real systems, there are at least minimal attractions between the molecules of the liquid and those of the solid. This interaction decreases the interfacial tension, so that  $\gamma_{sl} < \gamma_{lv} + \gamma_{sv}$ . The extent of the decrease is a direct measure of the strength of the interfacial attraction, and is termed the thermodynamic work of adhesion  $W_a$ :

$$W_a = \gamma_{lv} + \gamma_{sv} - \gamma_{sl} \quad (10)$$

This expression, first given by Dupre,<sup>61</sup> states that the reversible work  $W_a$  of separating a liquid and a solid must be equal to the free energy change upon separation.

Two different expressions for the thermodynamic work of adhesion may be obtained by combining Eqs. (4) and (10), or Eqs. (5) and

(10). In the former case,

$$W_a = \gamma_{lv}(1 + \cos \theta), \quad (11)$$

and in the latter,

$$W_a = 2\phi(\gamma_{sv}\gamma_{lv})^{1/2}. \quad (12)$$

When  $\gamma_{sv}$  and  $\gamma_{lv}$  are given values appropriate to simple nonpolar substances, about 25 mJ/m<sup>2</sup>, the value obtained for  $W_a$  from Eq. (11) or (12) is only about 50 mJ/m<sup>2</sup> or less. The actual work of detaching one adhering substance from another is found to be much larger than this, in the range 1 J/m<sup>2</sup> to 10 kJ/m<sup>2</sup>. Thus other contributions to the mechanical strength from dissipative processes within the adherends greatly outweigh the intrinsic adhesion. Nevertheless, these other contributions depend upon the existence of the intrinsic adhesion and they seem in some cases to be directly proportional to its magnitude.<sup>62,63</sup> If there is no affinity between the adherends, there is certainly no mechanical strength of an adhesive bond.

### Acid-Base Considerations

Another approach for describing solid-liquid interactions at an interface has been proposed, based on computations of acid-base interactions.<sup>64,65</sup> An empirical correlation exists for the enthalpy of mixing  $\Delta H_{AB}$  when an acid, i.e., electron pair acceptor, and a base, i.e., electron pair donor, are mixed:<sup>66-68</sup>

$$-\Delta H_{AB} = C_A C_B + \dot{E}_A E_B \quad (13)$$

Drago<sup>67</sup> assigned two empirical parameters to each acid ( $C_A$  and  $E_A$ ) and each base ( $C_B$  and  $E_B$ ), so that when substituted into Eq. (13) they give the correct  $\Delta H_{AB}$  for the acid-base pair. Heats of mixing were determined calorimetrically and could be correlated with infrared spectral shifts of groups involved in the acid-base interaction. Values of  $C$  and  $E$  can be used to predict  $\Delta H_{AB}$  for other acid-base pairs. Values of  $\Delta H_{AB}$  calculated in this way for a great variety of organic liquids agree very well with experimentally determined ones, usually within 5% or less. Upon mixing an acid and a base in

solution,  $\Delta H_{AB}$  is a direct measure of their mutual interaction.

Fowkes and coworkers extended Drago's methods to polymers and solid surfaces and have determined  $C$  and  $E$  values for them.<sup>69,70</sup> Furthermore, Fowkes suggested that acid-base interactions often dominate the attraction that occurs between a liquid and a solid. He proposed, in general, that the thermodynamic work of adhesion is given by<sup>65</sup>

$$W_a = 2(\gamma_s^d \gamma_l^d)^{1/2} + f(C_A C_B + E_A E_B)x + W_a^p \quad (14)$$

where the three terms on the right-hand side of Eq. (14) represent (1) nonspecific dispersive interactions, (2) acid-base or donor-acceptor interactions, and (3) a term to account for any electrostatic interaction not included in the second term.

$f$  = constant close to unity that converts enthalpy per unit area into surface free energy

$x$  = number of moles of acid-base interaction pairs per unit area of interface

$\gamma_s^d, \gamma_l^d$  = dispersive components of the surface tensions of the solid and liquid respectively.

Fowkes states that the first and last terms are often negligible.

## SURFACE TREATMENT

Solid adherends may have surface characteristics that would prevent the formation of a strong and durable joint. For this reason, surface treatments have been developed; these alter the surface region in one or more of the following ways: modify physical structure, change surface topography, change the chemical nature of surface, or remove a weak boundary layer.

Two materials which nearly always require surface treatment prior to adhesive bonding are metals and low energy polymers. These will be considered in turn.

## Metals

When a metal is processed, e.g., by a cutting or rolling action, the material near the forming device, now the surface region, is subjected to high stresses that can cause irregular local yielding and plastic deformation. This leads to an oxide which is less stable and less uniform compared to that which would have formed on a strain-free surface. Additionally, the oxide layer may be intrinsically weak or it may adhere poorly to the underlying metal. These conditions are often associated with an oxide layer that is too thick.

In order to prepare a metal surface for bonding, techniques have been developed that remove surface contaminants, the existing oxide layer, and some of the underlying metal as well. A new oxide with improved uniformity and strength is then formed under controlled conditions. Fig. 5 shows<sup>71</sup> an Auger spectrum for an "as-received" aluminum alloy (type 6061). Note the carbon signal indicative of contamination by organic species; also, the surface is rich in magnesium oxide, even though Mg only comprises 1.0% by weight of the alloy. Depth profiling<sup>71</sup> (Fig. 6) by sputtering reveals that the oxide thickness is about 1000 Å and organic species are quickly removed during sputtering.

It is important to note that surface contamination is not always detrimental to adhesive joint strength. In a recent study,<sup>72</sup> aluminum

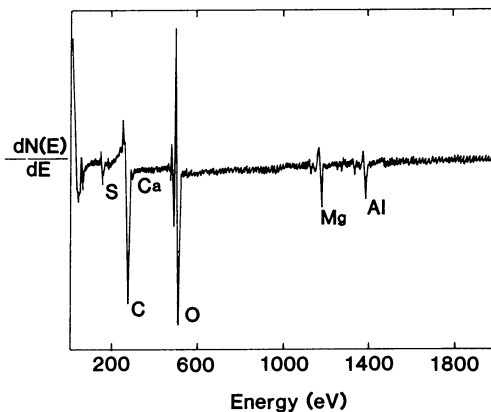


Fig. 5. Auger spectrum of aluminum alloy type 6061, "as received." (Taken from Ref. 71, published by Plenum Press.)

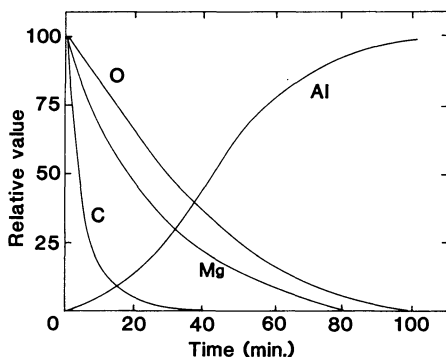


Fig. 6. Elemental depth profiles of the alloy of Fig. 5, obtained by ion beam sputtering. For each element, the ordinate is the peak-to-peak magnitude for the sputtered surface relative to its initial value. (Taken from Ref. 71, published by Plenum Press.)

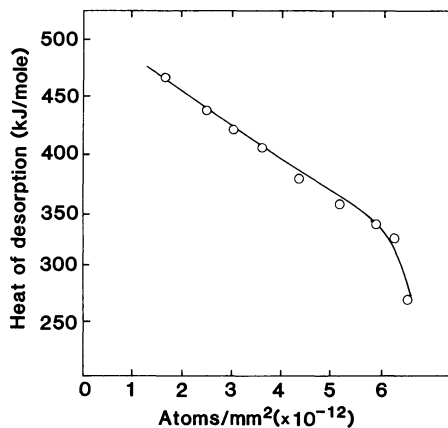


Fig. 7. Heat of desorption of sulfur from platinum as a function of surface coverage. (Taken from Ref. 73, published by Elsevier Science Publishers.)

adherends were purposely contaminated in a controlled way with either silicone oil or stearic acid before bonding with an epoxy adhesive. Although joint strengths were reduced with stearic acid contamination, they were influenced very little by silicone oil.

Vapor degreasing in a chlorinated solvent, ultrasonic cleaning, and exposure to elevated temperature have been used to remove surface contaminants, while chemical etching and mechanical abrasion are used to modify the nature of the oxide. An important consideration concerning removal of adsorbed contaminants is that the binding energy is greater at lower surface concentrations.<sup>73,74</sup> In consequence, as the adsorbed species is removed, more energy is needed to remove the remaining adsorbate. This effect is illustrated in Fig. 7, where the heat of desorption of sulfur from a platinum surface is seen to increase as the surface coverage decreases.<sup>73</sup> It is often quite difficult to remove the last traces of a contaminant.

Grit blasting is commonly employed to further modify a metal surface after degreasing.<sup>75</sup> The surface region is removed by the abrasive action of a stream of high velocity particles, such as silica or alumina. The resulting surface topography depends on the size and sharpness of the grit; high surface areas can result, which promote mechanical interlocking during bonding. Profilometer traces (Fig. 8) for aluminum (type 6061 T6) adherends that were either polished with diamond-dust paste or grit blasted

with 40- to 50-mesh  $\text{SiO}_2$  particles clearly show the roughening caused by the latter process.<sup>76</sup> A comparison of the effect of the two treatments on butt joint strengths with an epoxy adhesive is shown in Fig. 9. For test temperatures less than the  $T_g$  of the adhesive, joints made with grit blasted adherends have higher strengths. Bond strengths with either type of adherend are enhanced if an additional chemical etching treatment is used (see later).

Immediately after blasting, the freshly exposed metal will rapidly oxidize and begin to adsorb contaminants from the air. For this reason, it is often desirable, especially with sensitive metals like steel and copper, to coat the adherend immediately with a primer. This protects the surface and allows the item to be stored for a period of time before bonding, without sacrificing bond quality.<sup>75</sup> Additionally,

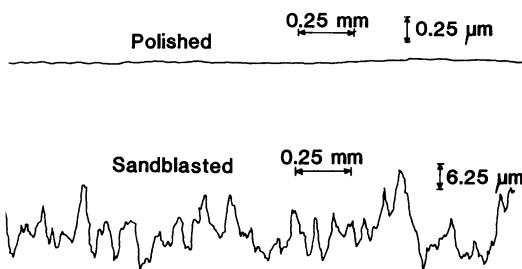


Fig. 8. Profilometer traces for an aluminum alloy (6061 T6) after polishing or sand blasting. (Taken from Ref. 76, published by Gordon and Breach Science Publishers.)

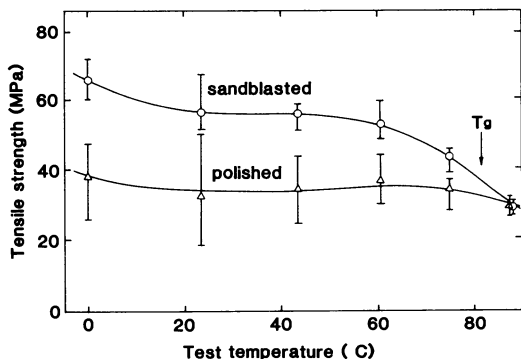


Fig. 9. Tensile strengths at various test temperatures for butt joints made with polished or sandblasted aluminum adherends and an epoxy adhesive. (Taken from Ref. 76, published by Gordon and Breach Science Publishers.)

primers have low viscosities so that they can readily fill surface crevices and irregularities.

We now consider some specific examples.

**Aluminum.** Aluminum to epoxy bonds have been studied intensively because of their importance in aircraft structures.<sup>79</sup> A surface treatment of vapor degreasing and grit blasting is sufficient to give an aluminum-epoxy lap shear joint that fails cohesively within the epoxy layer when stressed.<sup>78</sup> However, upon exposure to a moist environment, the joint strength declines markedly and failure occurs in the interfacial region. The strength decreases more rapidly if the joint is also stressed during exposure to humidity.<sup>79</sup> Fig. 10 illustrates this effect.<sup>80</sup> In a hot, humid environment aluminum-epoxy lap shear joints fell apart shortly after three years of exposure when loaded at 10% of the original breaking stress, whereas unstressed joints did not lose their strength so rapidly. Durable bonds with aluminum adherends require chemical treatments that provide a stable, high surface area oxide.<sup>81</sup>

A widely used treatment is the Forest Products Laboratory (FPL) process.<sup>82</sup> This consists of degreasing, alkaline cleaning, and etching in a solution containing  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{H}_2\text{O}$  in a 1 : 10 : 30 ratio by weight. Specimens are then thoroughly rinsed and air-dried. The type of water used in the rinse can also influence bond strength. In one study,<sup>83</sup> deionized water resulted in decreased bond strengths compared to rinsing in water containing diva-

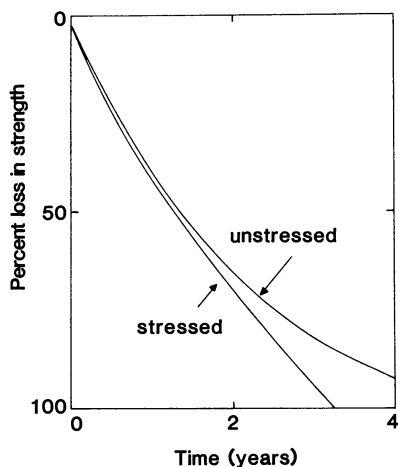


Fig. 10. Effect of stress during outdoor aging (hot, wet, tropical climate) on the residual strength of FPL-treated aluminum/epoxy lap shear joints. Lower curve gives results for joints which were stressed at 10% of the original breaking load during aging. (Data taken from Ref. 81.)

lent ions. AES analysis has shown that the oxide layer formed after rinsing in deionized water is much thicker than when tap water is used.<sup>84,85</sup>

During the etching, the original oxide is removed and typically about 1  $\mu\text{m}$  of underlying metal. The new  $\text{Al}_2\text{O}_3$  oxide<sup>86,88</sup> begins to grow during etching and then thickens somewhat during rinsing. SEM shows that the oxide consists of a uniform layer ca 50  $\text{\AA}$  thick next to the base metal with oxide spikes ( $\sim 50 \text{ \AA} \times 400 \text{ \AA}$ ) protruding outward.<sup>89,90</sup> This morphology provides a high surface area to enhance the extent of intrinsic bonding, and also results in mechanical keying of the adherend and adhesive. This gives excellent initial joint strengths.

In order to have a durable joint, it is necessary that the interfacial region maintain its mechanical integrity upon exposure to moisture. Davis and Venables<sup>89</sup> have shown that the primary mechanism for degradation of strength of an aluminum-epoxy joint during moisture aging is the conversion of the oxide to boehmite,  $\text{AlOOH}$ , which apparently is weakly bonded to the base metal. AES analysis of joints broken after exposure to high humidity has shown that fracture occurs at or near the boehmite-metal interface.<sup>89</sup>

Thus, to increase the durability of aluminum-epoxy bonds, it is necessary to form an oxide with enhanced stability to water. This has been accomplished by phosphoric acid anodization (PAA). The oxide formed by PAA is much thicker<sup>90</sup> than that produced by the FPL process. Additionally, the PAA oxide has an open cellular structure with a layer of  $\text{AlPO}_4$  on top.<sup>91</sup> The (barrier) phosphate layer is thought to be responsible for protecting the oxide from being converted to the hydroxide when a joint is exposed to moisture. Fig. 11 gives XPS results comparing the effect of humid aging on the aluminum 2p peak position for FPL and PAA treated surfaces.<sup>92</sup> Aging causes the peak to shift to lower binding energies for the FPL treatment—indicative of the oxide-to-boehmite transformation. Little change is seen with PAA samples. The very high surface area of the oxide coupled with its high stability result in aluminum-epoxy joints with outstanding strength and durability.

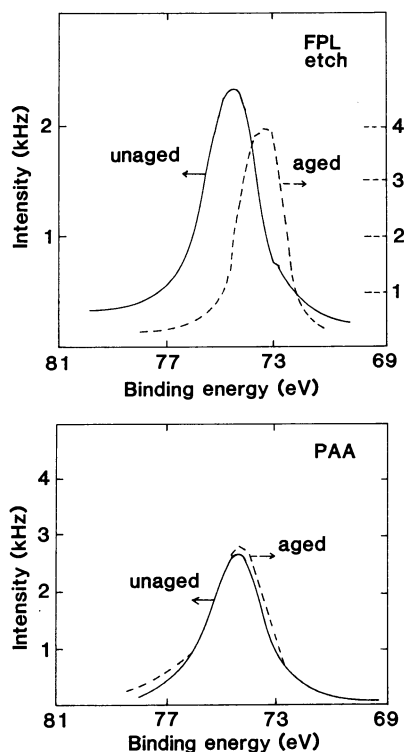


Fig. 11. Comparison of the Al 2p peak from XPS analysis for (a) FPL-etched and (b) PAA-treated aluminum, both initially and after aging one hour at 60°C and 100% R.H. (Taken from Ref. 92, published by Plenum Press.)

A new surface treatment<sup>93</sup> for aluminum adherends has been reported to give joints with epoxy adhesives that perform better in the Boeing wedge test than PAA-treated specimens. The process involves: degreasing, detergent cleaning, alkaline etching, nitric acid dipping, hard anodizing in 10% sulfuric acid, and finally dipping in phosphoric acid.

**Copper.** The bonding of polyethylene to copper provides another example of the importance of oxide topography on joint strength.<sup>94,95</sup> If the copper is first cathodically cleaned or chemically polished, then polyethylene adheres rather poorly. However, if the copper is given a wet oxidation treatment with sodium chlorate, sodium hydroxide, and sodium phosphate solution before bonding, then polyethylene adheres tenaciously. In the former cases, the oxide layer is rather smooth and uniform, whereas the last treatment produces a thick, black, dendritic oxide that adheres strongly to polyethylene by mechanical interlocking. The bond strength is enhanced by plastic deformation of the composite interlayer, consisting of the fibrous oxide embedded in polyethylene, which interlinks the bulk copper and polyethylene.<sup>96</sup>

**Steel.** Not all metal adherends require chemical surface treatments in order to give strong and durable joints. With mild steel, removal of soluble contaminants by vapor degreasing followed by grinding or grit blasting is sufficient.<sup>97</sup> However, the freshly created surface of steel is very reactive and reoxidizes almost instantly. It will continue to oxidize, especially in the presence of moisture, eventually forming a visible rust. The treated surface must be coated with a primer or adhesive before the oxide layer becomes too thick, otherwise joint strength and durability will be poor.<sup>98</sup>

## Polymers

Low surface energy solids such as polyolefins and fluorocarbon polymers are difficult to bond with conventional polar adhesives. Various methods have been developed to modify their surfaces to overcome this problem.<sup>99</sup> Common to all of them is surface oxidation.

**Corona Discharge.** Corona treatment is widely used with plastic films.<sup>100,101</sup> Exposure to the discharge is usually in air and at atmospheric pressure. Polyethylene treated in this way undergoes surface oxidation and some unsaturation is introduced.<sup>102</sup> This results in an increase in surface energy and wettability by polar adhesives, such as epoxies. Additionally, surface roughening takes place due to nonuniform degradation of the surface region.<sup>103</sup> This is thought to be caused by preferential attack at the more vulnerable amorphous portions compared to the crystalline regions. Enhanced joint strengths with corona-treated polyethylene are attributed both to increased surface roughness and to increased intrinsic adhesion with surface polar species including,<sup>104-106</sup> e.g., hydroxyl, aldehyde, carbonyl, and carboxyl groups. Fig. 12 gives XPS spectra for a corona treated surface of low density polyethylene.<sup>104</sup> The appearance of the O 1s peak indicates the formation of surface moieties containing oxygen. For a typical corona discharge treatment of polyethylene, these functional groups range in concentration from  $4 \times 10^{-3}$  to about  $1.4 \times 10^{-2}$  groups per surface methylene unit.<sup>104</sup>

Upon heating a corona-treated polyethylene sample to 85°C, it loses wettability and ability to bond.<sup>107</sup> This is attributed<sup>108</sup> to the polar groups turning inward toward the bulk material, leaving the surface with more of a hydrocarbon character. This process is facilitated at

high temperatures because of enhanced chain mobility.

**Acid Etching.** Surface groups introduced after chromic acid etching<sup>109</sup> of polyolefins are similar to those found after corona treatment. Surface roughening occurs as well.<sup>110</sup> Additionally, a small number of  $-\text{SO}_3\text{H}$  groups have been identified.<sup>41</sup> Increasing the etch time and temperature for polypropylene does not significantly change the degree of surface oxidation, but rather increases the depth to which oxidation occurs. In contrast, both the degree and depth of surface oxidation increase with etch time for polyethylene.<sup>41</sup> Only short etch times are required to obtain polyolefin-epoxy bond strengths that are comparable to the cohesive strength of the polyolefin. Extended etch times are detrimental to joint strengths, because of extensive degradation of the polymer.

The relative contribution of surface roughening compared to chemical oxidation on joint strengths has not been determined. This is a problem needing further research.

**Plasma Treatment.** A low-pressure activated-gas plasma, produced in an rf field, is employed.<sup>111</sup> When a polymer is exposed, active radicals and ions are created in the surface which lead to oxidation. Both inert gas (e.g., argon, helium) and reactive (e.g., oxygen) plasmas have been used although the latter is generally too active because of rapid and extensive degradation and ablation. (Oxygen plasmas are employed to remove organic contaminants from metals.) Plasma treatment increases the wettability and bondability of nonpolar polyolefins as well as polar plastics such as nylon, although in the latter case the improvement is modest.<sup>112,113</sup> An ammonia plasma treatment of polyethylene enhances bonding to cellulose (paper).<sup>114</sup>

There is some controversy regarding the mechanism of enhanced bondability after plasma treatment. In one study,<sup>115</sup> surface crosslinking was shown to occur during plasma treatment of polyethylene. This was proposed to strengthen the surface material, which was hypothesized to consist initially of a weak, low molecular weight fraction. Enhanced joint

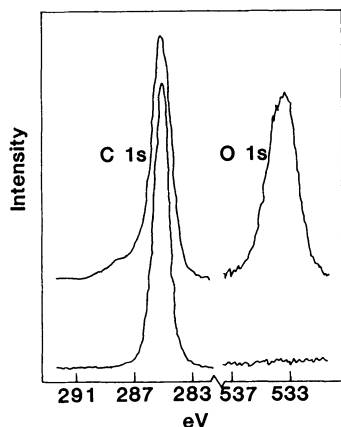


Fig. 12. XPS spectra of low density polyethylene before (lower curve) and after (upper curve) treatment in a corona discharge. (Taken from Ref. 104, published by Gordon and Breach Science Publishers.)

strengths were attributed to the elimination of this weak boundary layer. It must be noted, however, that the existence of a weak boundary layer on polyethylene surfaces has not been demonstrated conclusively. Nor has fracture within such a layer been shown to occur upon stressing an adhesively bonded polyethylene joint. On the contrary, fracture of a bond between untreated polyethylene and an epoxy adhesive occurs cleanly at the interface, and not within a polyethylene surface layer.<sup>41</sup>

Others feel the reason for increased joint strengths after plasma treatment is the introduction of polar functionality (oxidation) and enhanced surface energy.

**Other Methods.** In the three previous methods described for treating polymers, surface oxidation took place. Other direct methods of oxidation have also been used to modify polymer adherends effectively. With flame treatment<sup>116,117</sup> in air, an oxidizing flame briefly ( $\sim 0.01$ – $0.1$  sec) impinges on the surface. XPS analysis<sup>118</sup> has shown that amide surface groups are generated as well as typical oxidation functionality. Treatment by a blast of hot air has also been used to create surface macro-radicals that then combine with oxygen.

If a sensitizer such as benzophenone is added to the polymer, sufficient oxidation can occur simply by exposure to ultraviolet light. In this photochemical treatment, creation of polymeric radicals by proton abstraction occurs readily with the formation of the highly resonance-stabilized diphenylhydroxymethyl radical.

Rather than allowing the active species formed in a surface to combine with ambient oxygen, it is possible to have a reactive monomer present and form grafts to a surface.<sup>119,122</sup> In one study, radicals and ions were created in a polyethylene surface by irradiation with  $\gamma$ -rays in the presence of vinyl acetate monomer. The resulting polyethylene-vinyl acetate graft showed excellent bonding with an epoxy adhesive. Other researchers<sup>122</sup> have grafted acrylic acid onto polyethylene using electron irradiation. The greatly enhanced adhesion of the modified polymer to aluminum is shown in Fig. 13.

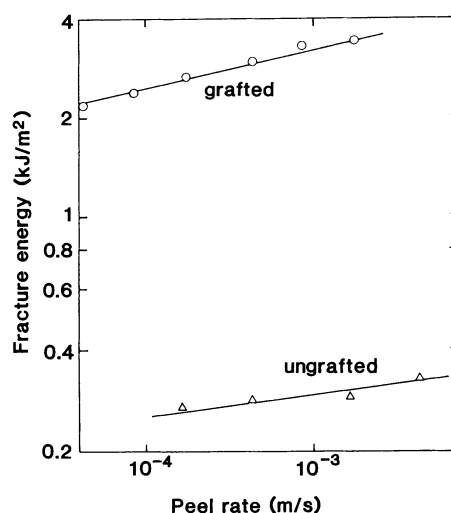


Fig. 13. Fracture energies of polyethylene and polyethylene-g-acrylic acid bonded to an aluminum plate. (Taken from Ref. 122, published by Butterworth Scientific.)

**Fluorocarbon Polymers.** Fluorocarbon polymers require treatment with powerful etchants before they can be strongly bonded. Metallic sodium dissolved in either a mixture of naphthalene and tetrahydrofuran, or in liquid ammonia is effective.<sup>123,124</sup> These reagents reduce the polymer surface by defluorination.<sup>125</sup> Initially, the surface is discolored, and it will form a carbonaceous black residue if treatment is continued too long. XPS analyses have shown the presence of unsaturation and carbonyl and carboxyl functionality after treatment.<sup>125</sup> Wettability and joint strengths are dramatically improved.

An interesting technique to improve the bonding of an epoxy adhesive to polytetrafluoroethylene (PTFE) has been demonstrated.<sup>126,127</sup> Two adherends are abraded in the presence of liquid adhesive. These are then brought into contact and the adhesive allowed to set. The shear strength of the joint is about seven times that obtained if the adherends are abraded in air before applying the adhesive. Presumably, when abrasion is carried out in the presence of the adhesive, active species are created in the PTFE surface due to chain rupture and they react directly with the adhesive. When abrasion takes place in air, these species may decay away before the adhesive is applied.



## MEASUREMENT OF ADHESION

### Introduction

Earlier portions of this review dealt with aspects of making adhesive bonds. We now consider methods of measuring adhesion. Many test methods have been developed but not all of them are amenable to analysis, i.e., to determining the relation between the breaking load, the dimensions of the components, and the properties of the adhesive and adherends. Even for the simplest cases this problem has proved to be quite difficult. Indeed, it is only recently that general fracture criteria have been developed and applied to simple joints.

**Energy Criterion for Failure.** It is first necessary to identify an initial site for separation to begin, usually at a defect or region of high stress at the interface. We then set up an energy balance, in which changes in strain energy in the stressed joint, and potential energy in the stressing device, are equated to the energy required for debonding. This equation constitutes our criterion for fracture: a joint will fail when, by growth of an initial defect or debond, enough mechanical energy is released from the system to meet, or exceed, the energy requirements for debonding. The strength of a number of simple adhesive joints is discussed below, using this basic concept of fracture mechanics.

An alternative method of analyzing the strength of a bonded assembly is to evaluate the stresses set up at the site of fracture and assume that rupture will occur when a critical level of stress is reached there. In principle, this method is equivalent to an energy criterion for fracture but energy calculations are often easier to carry out. Energy methods are used here exclusively, for this reason.

Notice that an implicit assumption is made that energy is not dissipated in irreversible processes other than fracture. Whatever energy is applied to deform the components is assumed to be fully regained when the deformation is removed. Although this assumption can be relaxed to take into account some plastic or viscous response, the analysis is simpler and more straightforward if the components are ideally elastic.

But this feature need not extend right up to the fracture plane itself. If the materials become dissipative at high stresses, in the immediate neighborhood of the crack tip; for example, if micro-cracking occurred there or if the yield stress was exceeded locally; then energy dissipated around the fracture plane can still be lumped together with that actually expended in molecular fracture as an overall *fracture energy* characteristic of the joint. Materials for which these assumptions are valid are termed *brittle*, even though they may be ductile locally, at the fracture site. Their strength is characterized by the amount of energy  $G$  required to propagate a crack through unit area. For interfacial failure of an adhesive joint the corresponding measure is the amount of energy  $G_a$  required to separate the adherends per unit area of interface. Obviously, if the strength  $G_a$  of the bond is greater than the strength  $G_c$  of an adherend, then the bond itself will not fail but the weaker adherend will split apart under sufficiently high stresses. This form of failure is termed *cohesive*, to distinguish it from simple interfacial failure, termed *adhesive*.

Energy considerations were first applied to the fracture of brittle solids by Griffith<sup>128</sup> and have since been applied to the adhesion problem by Rivlin and many others.<sup>129-145</sup> Notable recent contributions by Williams<sup>132,133,137</sup> and Kendall<sup>138-140</sup> form the basis for the present discussion.

### Test Methods

**General Considerations.** Ideally, a test method should have the following features. First, it should employ simple, easily prepared specimens. Secondly, the failure force should remain constant, at least in principle, as the line of separation is forced to advance over long distances, so that fluctuations in the failure force can be attributed to variations in the strength of adhesion. And, finally, the fracture energy  $G_a$  should be obtained directly from the dimensions of the specimen, its stiffness during loading, and the applied force at which failure takes place. No other measurements should be needed to calculate  $G_a$ .

A number of test methods are described here.

Attention is drawn to those that do not conform to the above requirements, although they may well have other advantages that make them useful tests. As a purely practical matter, some tests are particularly suitable for soft adhering layers, such as pressure-sensitive adhesive tapes, and others are more appropriate for "rigid," structural adhesives. This aspect should be obvious from the discussion in each case.

**Peeling.** One of the simplest and most widely used methods of measuring adhesion is by peeling a thin adhering layer away from a rigid substrate (Fig. 14a) or from an identical layer (Fig. 14b). The peel force is a direct measure of fracture energy, at least in the simplest cases, as the following analysis shows.

During steady-state peeling, conservation of energy requires that:

Work done by the peel force = work of detachment + strain energy imparted to the newly detached portion.

(15)

For peeling apart a unit length of bonded interface, Fig. 15, Eq. (15) becomes<sup>136</sup>

$$P(1 + e - \cos \theta) = G_a + tU \quad (16)$$

where  $P$  is the peel force per unit width,  $t$  is the thickness of the peeled strip and  $e$  and  $U$

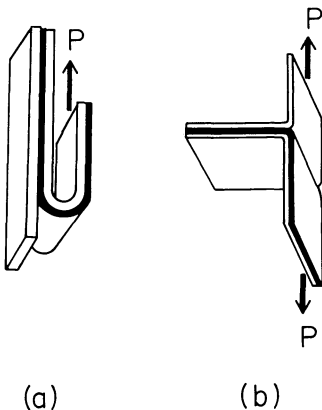


Fig. 14. Peel tests: (a) from a rigid base, (b) from a similar flexible layer.

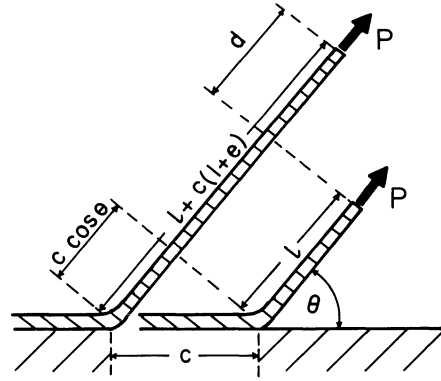


Fig. 15. Peel mechanics for an extensible adhering layer.

are, respectively, the tensile strain and energy density acquired by the detached strip. Adhering strips are generally thick enough to detach without stretching significantly, at least at peel angles of about  $45^\circ$  or more, so that  $e$  and  $tU$  are relatively small. In this case, Eq. (16) can be simplified and the peel force becomes

$$P = G_a / (1 - \cos \theta). \quad (17)$$

One further comment is necessary about Eq. (17). It is based on the assumption that no energy is expended in *bending* the strip away. And yet all materials are imperfectly elastic to some degree, and some of the work of deforming the sharply bent portion at the peel front will not be returned as the peel front moves on. Instead, it will be lumped in with the work of detachment and lead us to overestimate the true fracture energy  $G_a$ . And this error will be greater at larger peel angles, or with particularly dissipative materials, used either as adhesives or as backings.<sup>146</sup> It is therefore advisable to use small peel angles, but not so small that *stretching* of the layer becomes significant. A peel angle of  $45^\circ$  appears to be a good compromise.<sup>146</sup> With these reservations, the peel test is a satisfactory method of measuring the fracture energy of adhesion for a wide variety of flexible layers, tapes and films.

Of course, the same features that add to the work of detachment, and lead us to overestimate the value of  $G_a$  at large angles, can be exploited to enhance the resistance of adhering layers to peeling separation. Indeed, a large

fraction, over one-half, of the peel strength of commercial tapes appears to consist of plastic deformation of the backing material. We shall find repeatedly that an understanding of the mechanics of adhesive failure gives insights into possible ways of improving the strength of a joint, even if the true fracture energy of the interface is unchanged.

**Lap Shear.** When a stretchable adhering layer is pulled off parallel to the bond plane (Fig. 16) it will become stretched after detachment. For a linearly elastic strip the relation for the detachment force  $P$  per unit width is obtained from Eq. (16) as

$$P^2 = 2tEG_a \quad (18)$$

where  $t$  is the thickness of the strip and  $E$  is the tensile modulus of elasticity. The product  $tE$  thus represents the tensile stiffness of the strip per unit width.

In terms of the mean shear stress  $\sigma_s$  required to break the joint, Eq. (18) takes the form:

$$\sigma_s^2 = 2tEG_a/L^2 \quad (19)$$

where  $L$  is the length of the overlap. It is clear that a smaller mean stress will be required to break a lap-shear joint with a longer overlap.

Now this prediction is inconsistent with the idea that joints fail in shear at a critical level of mean shear stress. It is therefore important to know whether lap-shear joints do, indeed, fail at lower stresses for longer overlaps, because this finding would confirm the validity of a fracture energy criterion and disprove the validity of a critical mean shear stress criterion for failure. As engineering designs are based on failure criteria, it is important to know which one is correct.

As far as can be ascertained, the predictions of Eq. (18) appear to be valid.<sup>142</sup> Corrections must be made for short overlaps, when the ad-

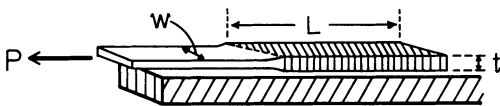


Fig. 16. Lap shear experiment: detachment of an extensible adhering layer at an angle of peel of  $0^\circ$ .

hering plates undergo bending as well as stretching,<sup>139</sup> but these are relatively minor. Moreover, the unexpected dependence of the breaking force and stress on the *thickness*  $t$  of the adhering layer, Eq. (18), is satisfactorily confirmed by experiment.<sup>139</sup>

A further, and convincing, demonstration of the validity of energy considerations is that the value of fracture energy  $G_a$  deduced from lap-shear measurements by means of Eq. (18) are in good agreement with values obtained from quite different experiments, for example, from peeling, Eq. (17). Thus, it appears that the energy criterion for fracture is appropriate and effective in accounting for the major factors governing breaking loads of lap shear joints.

**Tensile Detachment.** We consider first the detachment of an elastic half-space from a rigid plane, Fig. 17. If a circular debond of radius  $a$  is present at the interface, the tensile stress  $\sigma_b$  that will cause it to grow is given by

$$\sigma_b^2 = 2\pi EG_a/3a \quad (20)$$

where  $E$  is the tensile modulus of the adhering material. This result is exactly analogous to the relation for the tensile breaking stress of a bar of a solid material containing a small penny-shaped crack of radius  $a$  in its interior,<sup>147</sup>

$$\sigma_b^2 = \pi EG_a/3a \quad (21)$$

The same result, Eq. (20), is obtained for growth of a pressurized debond (a blister) of radius  $a$  at the interface between an elastic half-space and a rigid plane,<sup>137,148</sup> at least for an incompressible material. In that case, a tensile stress  $\sigma_b$  acting at infinity is exactly equivalent to a pressure of equal magnitude inside the blister.

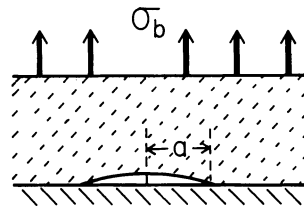


Fig. 17. Tensile detachment of a thick elastic layer with a circular interfacial debond, radius  $a$ .

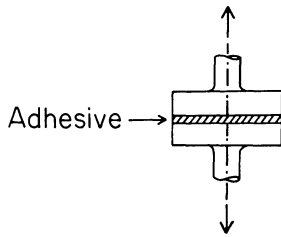


Fig. 18. Tensile detachment of a thin elastic (adhesive) layer.

When the adhering layer is thin, however, comparable to the blister radius, then the results are quite different because the deformation is then largely bending and biaxial stretching. This situation is discussed later.

Another common type of tensile test involves pulling apart two flat rigid plates with a layer of adhesive sandwiched between them, Fig. 18. This experimental arrangement is amenable to analysis by finite-element methods,<sup>149</sup> but the relation obtained for breaking load as a function of fracture energy appears to depend strongly upon the relative thickness (shape factor) of the adhesive layer as well as upon the dilatancy of the adhesive under stress. Indeed, as the thickness is decreased, the location of failure initiation changes, first from the edge to the center of a bonded interface,<sup>149</sup> and secondly, for soft, strongly adhering layers, to the center of the adhesive itself, where the material fails cohesively.<sup>150</sup> Thus, although they are fairly easy to carry out, interpretation of tensile tests is not a simple matter.

They also suffer from a major scientific drawback. Because the failure load decreases as the debond grows in size, failure is autocatalytic. Thus, once the conditions are set up for an initial defect to grow, it will propagate at an ever increasing rate until the specimen is completely broken. Experiments at a known and controllable speed are thus hardly feasible. Additionally, the origin of failure is a chance flaw or debond of unknown size (unless care is taken to introduce known, reproducible defects), and thus one of the essential parameters in the relation for the failure stress, Eq. (20), is unknown.

**Torsional Fracture.** A particularly attractive test for structural adhesives is the con-

trolled splitting apart of two plates or beams, bonded together along one edge, by twisting them about an axis passing through the adhesive, as proposed by Outwater.<sup>134</sup> This can be achieved by applying bending loads to one end of the bonded specimen, as sketched in Fig. 19, or by applying a torque with a pulley arrangement as sketched in Fig. 20. The latter is experimentally more convenient,<sup>145</sup> but the principle is the same. At a critical value of applied load  $P$ , denoted  $P_c$ , or torque  $M$ , denoted  $M_c$ , an initial crack of length  $c$  made between the two adhering plates will advance. At this point, elastic energy stored in the two twisted arms begins to be expended in fracture. If we assume that the cleaved arms of the specimen are linearly elastic in torsion, and that their torsional stiffness is inversely proportional to the

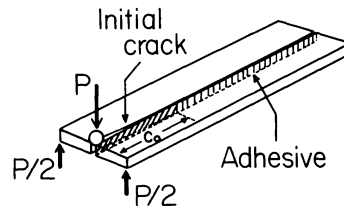


Fig. 19. Double-torsion experiment: direct loading for small torsions.

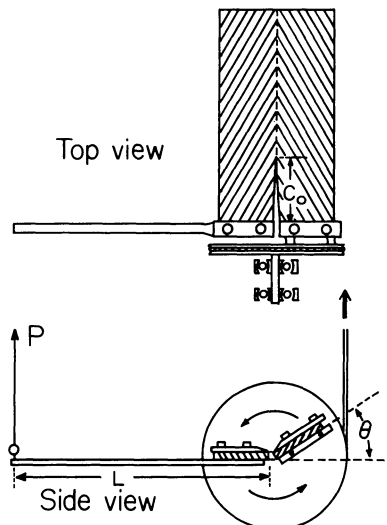


Fig. 20. Double-torsion experiment: use of pulley and beam for large torsional deformations. Torque  $M = PL$ . (Taken from: K. Cho and A.N. Gent, *Internatl. J. Fracture*, **28**, 239 (1985), published by Kluwer Academic Publishers.)

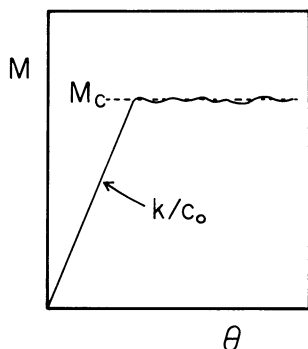


Fig. 21. Relation between applied torque  $M$  and angle of rotation  $\theta$  for a double-torsion experiment, Fig. 20.  $M_c$  denotes the critical value of torque at which fracture propagates. (Taken from: K. Cho and A.N. Gent, *Internatl. J. Fracture*, **28**, 239 (1985), published by Kluwer Academic Publishers.)

length  $c$  of the arms, we can obtain the fracture energy  $G_a$  from an energy balance, in the form<sup>134,145</sup>

$$G_a = M_c^2 / 2kt \quad (22)$$

where  $k = Mc/\theta$  is a constant denoting the torsional stiffness of the specimen for a crack of unit length, and  $t$  is the thickness of the cleaved bond. The value of  $k$  can be obtained from the experimental relation between torque  $M$  and angle  $\theta$  of rotation up to the onset of fracture, Fig. 21, and the mean value of  $M_c$  can be measured thereafter, over long distances for long test pieces. Thus, the mean fracture energy  $G_a$  can be measured with some confidence, using a single specimen of simple design.

**Cleavage.** Another test method used widely for stiff, structural adhesives involves pulling apart two stiff cantilever beams bonded together with a thin layer of adhesive, Fig. 22. In this case, bending energy stored in the bent arms is released as the crack advances. Again, we can obtain a relationship from energy considerations between the failure force  $P$  applied to cleave apart the specimen, the dimensions and bending stiffness of the beams, and the fracture energy  $G_a$ :

$$P^2 = EIG_a/c^2. \quad (23)$$

In this relationship,  $I$  denotes the second moment of area of a beam cross-section ( $I =$

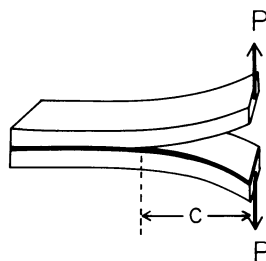


Fig. 22. Double-cantilever experiment.

$wt^3/12$  for beams of rectangular cross-section) and  $c$  denotes the distance between the point of application of the load and the crack front, Fig. 22. In order to obtain a constant failure force, at least in principle, as the crack advances, specially prepared beams can be made with cross-sections that change in such a way that the bending rigidity  $EI$  increases appropriately with  $c$ .

**Pull-Off Test.** This simple test is shown in Fig. 23. An adhering strip is pulled away from a rigid substrate by a force  $P$  per unit width. Work is expended in stretching the strip as it detaches, and in breaking the bond. Assuming again that the strip is linearly elastic and that the angle  $\theta$  at which it detaches is small, the relation between  $P$  and  $\theta$  is given by

$$P = Et\theta^3 \quad (24)$$

where  $E$  is the tensile modulus of the strip and  $t$  is its thickness. In terms of the fracture energy,

$$P^4 = 19.0 EtG_a^3. \quad (25)$$

Thus, if only the pull-off force  $P$  is measured, an independent measurement of the stiffness of the strip is needed in order to determine the fracture energy. However, a simple relation is obtained in terms of the product of the pull-off

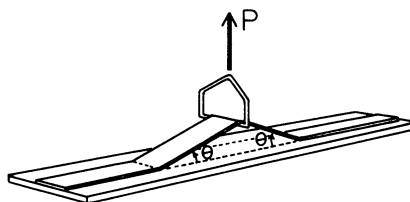


Fig. 23. Pull-off test.

force  $P$  and angle  $\theta$  of detachment, both of which remain constant, at least in principle, as detachment proceeds:<sup>145</sup>

$$G_a = \frac{3}{8} P\theta. \quad (26)$$

Thus, continuous measurements of fracture energy can be made from simple observations on a single specimen.

A notable feature of this experimental arrangement is the non-linear relationship that holds between force  $P$  and angle  $\theta$ , a measure of deformation, Eq. (24). Provided that the system is elastic, the principles of fracture mechanics can be applied to systems that follow nonlinear relations between load and deflection. Another example is given in the next section.

**Blister Tests.** Blister tests are appealing for measuring the adhesion of thin layers or films, (for example, of paint), to a rigid substrate, because they resemble failure processes encountered in service. Also, they can be analyzed theoretically to yield values of the fracture energy  $G_a$ . But they take several different forms. When the pressurized debond (blister) is small in radius compared to the thickness of the overlying layer, then the failure criterion is the same as that discussed previously under tensile tests, Eq. (20). When the blister radius is comparable to the thickness of the overlying layer, then the layer is deformed primarily in bending and the relation for the failure pressure  $\Pi$  becomes<sup>133</sup>

$$\Pi^2 = 128EG_at^3/9a^4 \quad (27)$$

where  $t$  is the layer thickness and  $a$  is the blister radius.

A third case, particularly important for thin films, is where the blister radius  $a$  is larger than the layer thickness  $t$ , Fig. 24. The principal mode of deformation of the layer is then biaxial stretching, and the relationship between inflating pressure  $\Pi$  and height  $y$  of the blister before any further detachment occurs is given by<sup>151</sup>

$$\Pi = 4.75Ety^3/a^4, \quad (28)$$

where  $E$  is the effective tensile modulus of the layer. By considering changes in strain energy

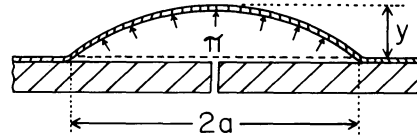


Fig. 24. Blister test.

as the blister grows, the pressure at which further debonding takes place is then obtained in terms of the fracture energy  $G_a$  of the interface<sup>152</sup>

$$\Pi^4 = 18.0EtG_a^3/a^4. \quad (29)$$

Note that the relationship between load and deflection is again a cubic one for small deflections of an inflated membrane, Eq. (28), even though the overlying layer has been assumed to be linearly-elastic. As a result, Eq. (29) for the failure pressure has an unusual three-fourths power dependence upon fracture energy, as in Eq. (25). And, again, if we measure simultaneously the failure pressure  $\Pi$  and the deflection  $y$  of the blister, then we obtain a particularly simple relationship for the fracture energy  $G_a$ <sup>145</sup>

$$G_a = 0.65\Pi y. \quad (30)$$

Thus, even though the blow-off pressure does not stay constant as the blister grows, Eq. (29), measured values can be employed with corresponding values of the blister height to calculate the strength of adhesion continuously; no other parameters are needed.

#### Pull-Out of Inextensible Rods and Fibers.

The strength of adhesion to the surrounding material is an important parameter for fibers or cords used as reinforcing components of composites. One method of measuring this property is by partially embedding the fiber or rod in a block of the matrix material and measuring the pull-out force  $P$ . A sketch of the experimental arrangement is shown in Fig. 25. By applying the principle of energy conservation during detachment the pull-out force  $P$  is obtained in terms of the interfacial fracture energy  $G_a$ <sup>153</sup>

$$P^2 = 4\pi a A E G_a \quad (31)$$

where  $a$  is the radius of the fiber and  $A$  is the cross-sectional area of the block in which the

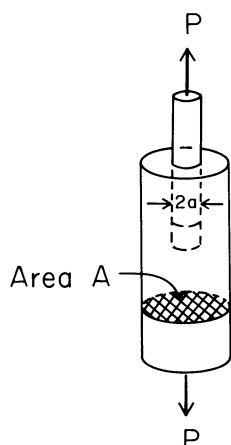


Fig. 25. Pull-out of an inextensible rod, radius  $a$ , from an elastic block, cross-sectional area  $A$ .

fiber is embedded. Experiments to test this relation have shown that it is obeyed satisfactorily for rods or fibers of small radius, but for larger radii or for deeply embedded fibers a large additional term in the energy equation arises from frictional resistance to pull-out.<sup>154</sup>

Provided that this term is not a major one, however, there are significant advantages in using a pull-out test to measure the strength of adhesion. The pull-out force remains constant, at least in principle, as the debond propagates along the length of the fiber, starting from the embedded tip. Moreover, even for strongly bonded fibers, fracture tends to follow the circumference of the fiber closely because, as Eq. (31) indicates, the pull-out force decreases as the radius  $a$  of the circular fracture front decreases. This test method is therefore particularly helpful when the strength of adhesion approaches the cohesive strength of the adhering material and the fracture plane tends to deviate from the interface into the adhesive itself.

When a number of fibers are embedded in a single elastic block and are all pulled out together, Fig. 26, then the work required for detachment is obviously larger than for a single fiber, by a factor equal to the number of fibers,  $n$ . The strain energy stored within the block must therefore be larger than before, by a factor of  $n$ , and the total force applied for pull-out must be increased, by a factor of  $n^{1/2}$ . Thus, energy considerations lead immediately to the surprising conclusion that the total force re-

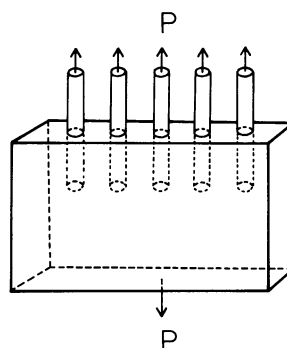


Fig. 26. Pull-out of  $n$  fibers simultaneously from a single block.

quired to pull out  $n$  fibers simultaneously from a single elastic block will increase in proportion to  $n^{1/2}$ . This prediction has been verified experimentally for 1–10 cords embedded in a rubber block, Fig. 27.<sup>153</sup> It provides a striking example of the success of simple energy calculations in accounting for important features of the strength of bonded joints and structures.

**Fiber Fragmentation.** An unusual way of estimating the strength of interfacial bonding for fine fibers is the single fiber tensile test.<sup>155</sup> Glass or carbon fibers used as reinforcing components in composites have diameters of only a few micrometers and it is difficult (although not impossible), to measure pull-out forces for such small fibers. An alternative method is to embed a fiber within a tensile bar of the matrix material, along the axis. On stretching the bar, the fiber, being less extensible, breaks in two.

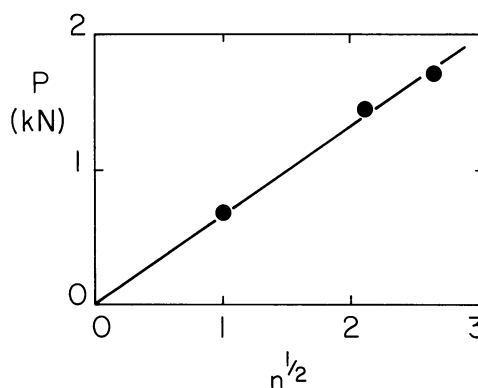


Fig. 27. Total pull-out force  $P$  for  $n$  fibers, pulled out simultaneously from a single block, vs.  $n^{1/2}$ . (Taken from Ref. 153, published by Chapman and Hall.)

Then, as the bar is stretched further the pieces of fiber break again, and so on until the fiber is fragmented into many small lengths. But, eventually a limit is reached at which the fiber fragments no longer continue to break as the bar is extended further. This state is shown schematically in Fig. 28.

Apparently, when the fiber length is small enough, the forces that can be transmitted to it by shear stresses from the adhering matrix material are no longer sufficient to break it. A simple force balance suggests that the strength of the interface, in terms of the maximum shear stress  $\sigma_a$  that it can transmit, is given by

$$\sigma_a = \sigma_b a / l_c \quad (32)$$

where  $\sigma_b$  denotes the tensile breaking stress for the fiber,  $a$  is the fiber radius, and  $l_c$  is the mean fragmentation length.

It is thus possible from observations of  $l_c$  to deduce the interfacial bond strength  $\sigma_a$ . Many such measurements have been reported.<sup>155-158</sup> But this criterion for fracture is not easily translated into energy terms. Indeed, it is quite likely that an energy criterion would take a different form from Eq. (32). (We recall the fracture analysis of a simple lap shear test, and the failure of a shear stress criterion for fracture to hold in that case.) The reader is therefore recommended to treat Eq. 32 as an interesting correlation between adhesion and observable features of stiff fibers in a more extensible matrix, but one that will probably be superseded when an energy analysis has been carried out.

**Needed Test Methods.** It is impossible to list, never mind discuss, all of the other methods that have been proposed for measuring adhesion. However, there remain serious needs, still unmet. One is for the accurate measurement of thin-film adhesion; for example, in microelectronics and biomedical applications. A detailed review of this subject has been given by Mittal,<sup>159</sup> but it appears that a generally sat-

isfactory test method has not yet been developed.

Another urgent requirement is for a *nondestructive* test for adhesion. Although there are a variety of ways of finding small debonds at interfaces (for example, by x-ray tomography), as far as the authors are aware there is no method presently available that can distinguish a weak, but defect-free, bond from a strong one, apart from breaking it.

## Conclusions

What, then, is the best method for measuring adhesion? For flexible materials, it is probably a peel test at a shallow angle of peel, around  $45^\circ$ , and with the precautions mentioned in the text. For a structural adhesive, the choice lies between a cleavage test and a torsion test, with the latter being slightly preferred. In both cases, it is essential that the adherends be within their elastic limit. Otherwise, the basic energy balance, on which a quantitative interpretation of the results depends, is invalid.

For films and tapes, a pull-off test seems appropriate. In this case, a stiff elastic backing can be applied to reinforce the adhering film, if it is not stiff enough or too plastic in tension. And the same trick can be used with adhering paint films, if they would otherwise be too plastic to treat as "elastic" layers.

## STRENGTH OF ADHESION

### Introduction

Values of the strength of real adhesive bonds, represented by the fracture energy  $G_a$ , can be determined by any of the methods described in the preceding section of this chapter. They are found to range from a few  $\text{J}/\text{m}^2$  to  $10,000 \text{ J}/\text{m}^2$  or more. We must now try to account for these differences. Why is a particular value of strength obtained with one formulation and not with another? The answer turns out to involve both molecular interactions across the interface and deformation processes within the adhesive.

Plastic yielding, flow, and other mechanisms of energy dissipation within the adhesive, near the failure site, are essential features of strong adhesives. Far from this region, however, the deformations are smaller and may well be vir-

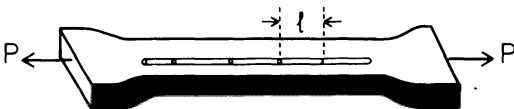


Fig. 28. Single-fiber fragmentation experiment.



tually elastic. For example, structural adhesives are able to carry sizeable loads without yielding, and yet there is every indication that they yield locally, before breaking, at points where the bond is highly stressed.

We turn now to the separate effects of interaction at the molecular level and irreversible local deformations.

### Molecular Interactions

It is plausible, but often misleading, to associate a strong bond with a strong interaction between materials on a molecular level. In fact, rather weak intermolecular bonds, for example, the London-Van der Waals bonds that exist in all substances, are sufficient to make strong materials and joints. The correlation between intrinsic strength of chemical bonds and mechanical strength of a substance, or of an interface, is often rather poor.

In order to seek a better correlation, we must first attempt to remove all dissipative mechanisms from the system. Otherwise, the bond will appear to be stronger than it really is, because of energy expended in processes other than molecular separation or rupture at the interfacial plane. So, for soft polymeric adhesives, the possibility of viscous flow must be eliminated. One way of doing this is by lightly linking the polymeric molecules together *in situ*. In this way their characteristic interaction with the substrate can be preserved, while they are prevented from flowing apart on separation.

A second step is necessary. Even crosslinked polymers have residual dissipative features due to internal motions of molecular segments, a type of "internal viscosity." It is therefore necessary to carry out the measurements of strength at very low rates of deformation and at high temperatures, far above the glass transition temperature, to minimize energy absorption from these processes.

Finally, the adhesive must consist only of the polymer itself (and possibly some compatible fluids). If reinforcing solid particles are present, they may cause energy to be dissipated in other ways, for example, by internal friction, dewetting of polymer from the particles, or separation of mutually adhering particles.

When all of these precautions are taken, it is

possible to make measurements of bond strength that approach a lower limit, termed *threshold strength*, that is due solely to molecular interactions between polymer and substrate across the interface. But, as can be readily understood from the stringent conditions that must be met, the number of adhesive materials that have actually been examined in this way is still very small.

**Threshold Strength.** Unfortunately, published measurements of threshold strength seem to be inconsistent. In one case, simple, lightly crosslinked polymers are reported to adhere under threshold conditions with a strength  $G_a$  of about  $0.1 \text{ J/m}^2$ , close to the value expected from London-Van der Waals bond energies.<sup>160</sup> In other cases, the threshold strength for similar polymers has been reported to be much larger, about  $1 \text{ J/m}^2$ .<sup>161</sup> Resolution of this discrepancy is clearly desirable. In the meantime, we note only that these values are extremely small, much lower than could be utilized in construction. For example, a strength of  $1 \text{ J/m}^2$  corresponds to a resistance to peeling separation at an angle of  $90^\circ$  of only 1 Newton (about 4 oz weight) per meter of bond width, and forces due to gravity would generally exceed this. Stronger interactions at the interface are therefore required to create a strong joint under threshold conditions.

**Chemical Coupling.** Various bifunctional materials are employed to link two materials together chemically. Probably the best known of these *coupling agents* are the silanes, designed to react both with OH groups on an inorganic substrate such as glass or metal and with reactive groups on the molecules of an adhesive resin.<sup>162</sup> The functional groups on silane molecules are chosen to react with the particular adhesive. Some examples are given in Table 1. Specific coupling agents have been developed for bonding glass fibers to polyester resins, carbon fibers to epoxy resins, and talc particles to Nylon. Virtually all glass fibers used in fiber-glass composites are silane-treated, and the resistance to deterioration by hot water is greatly enhanced in this way.

A simple example of a coupling agent is tri-

**Table 1. Silane Coupling Agents.**

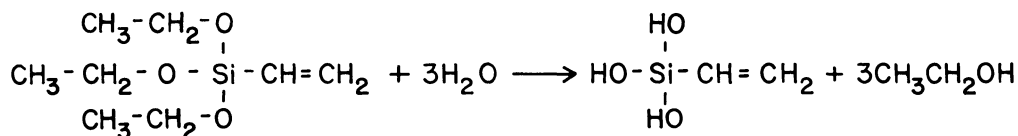
Type	Formula	Used With
Vinyl triethoxysilane	$\text{CH}_2=\text{CHSi}(\text{OCH}_2\text{CH}_3)_3$	crosslinked polyethylene, thermosetting polyester, diene elastomers
$\gamma$ -glycidoxypropyltrimethoxy silane	$\text{CH}_2\text{OCHC}-\text{H}_2\text{O}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$	epoxy, urethane, polyvinylchloride, phenolic
$\gamma$ -aminopropyltriethoxysilane	$\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_3)_3$	epoxy, melamine, nylon, polycarbonate, polyimide
$\gamma$ -mercaptopropyltrimethoxysilane	$\text{HSCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	epichlorohydrin, urethane, polyvinylchloride

ethoxyvinylsilane, Fig. 29. This substance hydrolyzes to yield silanol groups, and they are thought to condense with OH groups on a suitable substrate, for example, on glass, Fig. 29b, to form strong chemical bonds. When a polymer having a vinyl group in the molecule is applied to a silane-treated surface, it is then possible to interlink the two vinyl groups, at least in principle, as shown schematically in

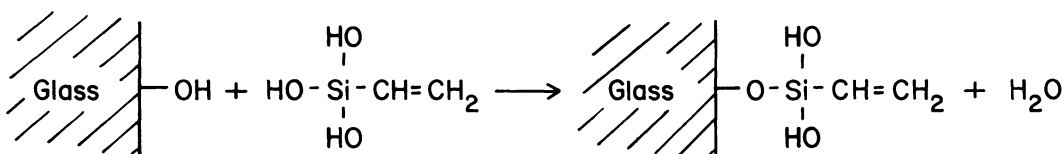
Fig. 29c, and thus introduce chemical bonds between polymer and substrate.

Measurements show that silane interlinking increases the threshold strength enormously, Fig. 30, to approach the intrinsic (threshold) strength of the polymer. But that is only of the order of 20–100 J/m<sup>2</sup>.<sup>161</sup> Obviously, the inherent strength of real adhesive bonds must be further enhanced by dissipative processes.

### (a) Hydrolysis



### (b) Condensation



### (c) Coupling

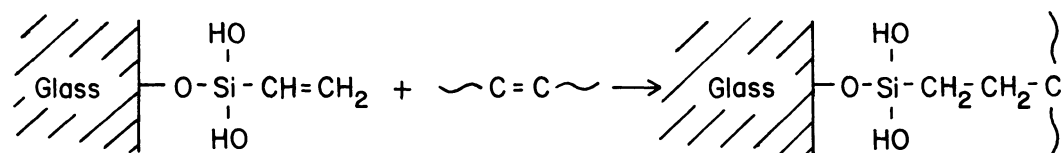


Fig. 29. (a) Triethoxyvinylsilane; (b) condensation on glass; (c) reaction with a diene polymer.

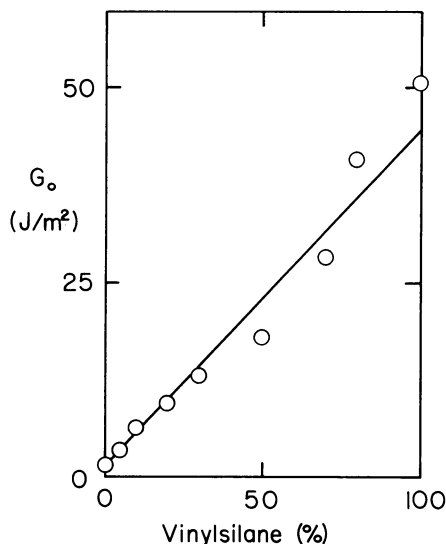


Fig. 30. Threshold strength of adhesion for a polybutadiene layer adhering to glass treated with varying proportions of triethoxyvinylsilane. (Taken from Ref. 161, published by John Wiley & Sons.)

### Rheology of Soft Adhesives

**Rate and Temperature Effects.** Adhesion of a soft crosslinked polymer to a rigid substrate is found to increase markedly as the rate of debonding is increased. An example is shown in Fig. 31. The strength also increases as the temperature is reduced, Fig. 31. Thus,

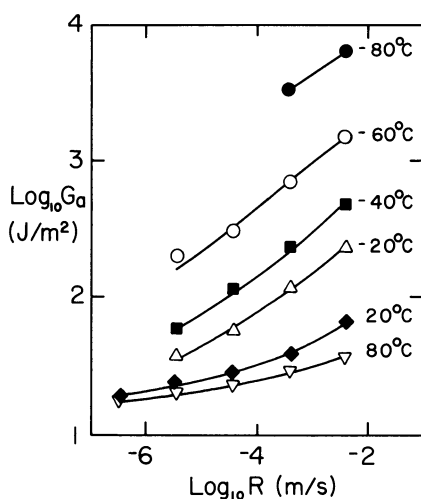


Fig. 31. Strength of adhesion of a polybutadiene layer to glass treated with a silane mixture vs. rate of peeling at various temperatures. (Taken from Ref. 161, published by John Wiley & Sons.)

as we move away from threshold conditions to higher rates and lower temperatures, the measured strength of a bond rises, often by large factors. This explains how chewing gum, for example, can adhere strongly, even though it has little inherent adhesion, because it deforms in a nonequilibrium way under normal circumstances.

In fact, the same increase in joint strength that is obtained with a simple viscoelastic adhesive on increasing the rate of debonding, can be achieved by a suitable reduction in test temperature. This is referred to as the principle of rate-temperature equivalence. For amorphous glass-forming liquids above their glass transition temperature  $T_g$ , Williams, Landel, and Ferry (WLF) proposed a universal relationship for the ratio  $a_T$  of corresponding test rates at temperatures  $T$  and  $T_g$ :<sup>163</sup>

$$\log_{10} a_T = 17.4(T - T_g)/(51.6 + T - T_g) \quad (33)$$

The factor  $a_T$  also represents the ratio of the rates of Brownian motion of molecular segments at  $T$  and  $T_g$ , and this is the theoretical basis for the WLF relation.

An example of the utility of this relationship is given in Fig. 31. The fracture energy  $G_a$  is plotted as a function of peeling rate at several temperatures, for an elastomeric layer adhering to glass. As can be seen, the results for each temperature give parallel curves when plotted against the logarithm of peel rate and they can be shifted along the log rate axis to bring them into superposition, Fig. 32.<sup>161</sup> The displacements  $\log a_T$  required to do this are found to be in good accord with Eq. (33), indicating that the temperature dependence of adhesion reflects corresponding changes in the rates of motion of molecular segments. It has nothing to do with the thermodynamics of wetting and adhesion, therefore, but is instead related to kinetic factors, probably viscous loss processes as the adhesive layer is pulled away from the substrate.

After superposition, the results form a master curve, Fig. 32, giving the fracture energy at any desired temperature (in this case  $T_g$ ) as a function of the equivalent rate of peeling at that

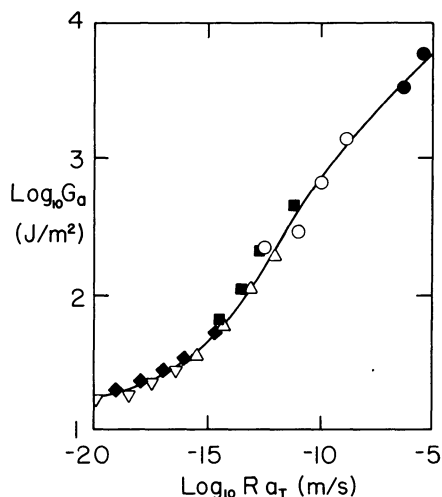


Fig. 32. Master curve relating the strength of adhesion to the effective rate of peeling at  $T_g$  ( $-95^\circ\text{C}$ ). Results taken from Fig. 31.

temperature. Thus, it is possible to deduce the dependence of the fracture energy upon rate of peeling over a wide range, using only limited data obtained over a narrow range of rates, but at a number of temperatures.

It must be emphasized that the WLF equation is only applicable to simple viscoelastic substances. It does not hold for semicrystalline or glassy adhesives. Nevertheless, it reveals the importance of internal dissipative processes in the work of detachment.

The mechanical response (elastic modulus and fracture energy) of certain epoxy and rubber-modified epoxy adhesives as a function of test rate and temperature have been shown to superpose to form single master curves. Here, however, the shift factor  $a_T$  is not a universal function of temperature; it must be determined empirically for each adhesive type. Much research is still needed before a good understanding is reached of the rate and temperature dependence of the strength of glassy adhesives. The effects are generally smaller, however, than for pressure-sensitive adhesives, above their glass transition temperatures.

**Adhesion on Contact.** Some adhesives have the special property (adhesive tack) of sticking firmly after brief contact under a light pressure. Thus, they wet the surface quickly,

like a mobile fluid, and yet resist detachment as if they had been transformed rapidly into a cohesive solid. These apparently contradictory features can be achieved by careful control of the physical properties of the adhesive. First, to secure rapid wetting the adhesive must be compliant. It is recommended that the compressive compliance after 1 sec under load be greater than about  $10^{-6} \text{ m}^2/\text{N}$ .<sup>164</sup> Then the forces of attraction between molecules of the adhesive and substrate are sufficient to pull the adhesive into intimate contact, even when the substrate surface is irregular on a microscopic scale.

Secondly, when the adhesive is about to detach, it is subjected to quite high stresses at the tip of an interfacial separation. If it is able to flow like a yielding solid, then the separation front is blunted, the stresses are minimized, and separation is prevented. Moreover, if the adhesive also hardens at high strain levels to become a tough solid, the adhesive layer itself cannot easily be ruptured. Thus, a substance which flows readily at low stresses but hardens at high levels of strain is potentially effective as a pressure-sensitive adhesive. Some elastomers are self-strengthening by virtue of the steric regularity of their molecules which allows them to crystallize rapidly on stretching. *Cis*-polyisoprene (natural rubber), *trans*-polychloroprene (Neoprene), and polyisobutylene all have the property of crystallizing at high strains, and all of them have been employed in pressure-sensitive adhesive formulations.

Thus, the requirements for a successful pressure sensitive adhesive formulation are that it must possess little resistance to small strain deformation, so that rapid wetting takes place, and yet it must also be able to support large strains without flowing apart easily. These features are obtained by a loose network of high-molecular-weight entangled molecules, diluted with special resins (tackifiers).

**Tackifiers.** Tackifiers are materials that are added to elastomers to improve contact adhesion. They generally have molecular weights in the 500–2000 range, with broad molecular weight distributions. Their softening points vary from 50 to  $150^\circ\text{C}$  and they often have

rather limited compatibility with the elastomer to which they are added.<sup>165,166</sup> Common tackifiers include rosin derivatives, coumarone-indene resins, terpene oligomers, aliphatic petroleum resins and alkyl-modified phenolics.

The effect of adding tackifiers on the rheological properties of elastomers is instructive in understanding how a tackifier functions. Fig. 33 shows a plot of the shear storage modulus,  $G'$ , of natural rubber with and without a tackifying resin.<sup>167</sup> When the resin is present the resistance to deformation is reduced (lower  $G'$ ) at low rates, and hence bond formation is facilitated on contact. At the same time, when measuring the strength of the bond at higher rates of deformation, the modulus  $G'$  is high and the material is stronger. This behavior can be contrasted with the effects of adding a filler or plasticizer. Fillers cause an increase in elastic modulus, but this is offset by the difficulty in bond formation. Also, while plasticizers promote bond formation, the cohesive strength of the adhesive is lowered. A tackifier is thus an appropriate compromise substance that allows an increase both in the ease of bond formation and in the elastic modulus and hence strength during detachment.

**Rate and Temperature Effects for Pressure-Sensitive Adhesives.** Pressure-sensitive adhesives consist of soft elastomeric semi-solids. Their peel strength depends strongly upon the rate of peel and the test tem-

perature, as shown for a simple model system in Fig. 34.<sup>168</sup> At low rates the peel force increases with rate, and failure takes place entirely within the adhesive layer, which fails by flowing apart. At a critical rate of peel (which depends upon the test temperature) an abrupt transition takes place to interfacial fracture, i.e., apparently clean separation of the adhesive from the substrate, at much smaller peel forces. This transition occurs when the rate of deformation of the adhesive layer at the peeling front becomes so high that the adhesive molecules are unable to disentangle and flow apart, like a liquid, but remain intertwined as a coherent elastic solid. Although the local stress required to disentangle the molecules at low rates is relatively small, the work expended in ductile flow is large and the peel force (which measures the work of separation) is correspondingly high. In the elastic state, the work of separation is mainly expended near the interface, and is then relatively small.

The rate of peel and test temperature at which the abrupt transition occurs are directly dependent upon the rate of Brownian motion of molecular segments. Simple viscoelastic adhesives therefore obey the WLF rate-temperature equivalence, Eq. (30), as shown in Fig. 35. The peel strength above the critical rate depends upon factors discussed previously: interfacial attractions and dissipative processes within the adherends. Below the critical rate, the peel strength is primarily a measure of the work of

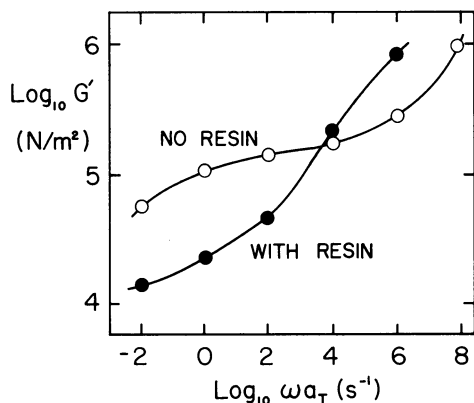


Fig. 33. Effect of a tackifier on the dynamic modulus  $G'$  of natural rubber as a function of reduced deformation frequency  $\omega a_T$ . (Taken from Ref. 167, published by John Wiley & Sons.)

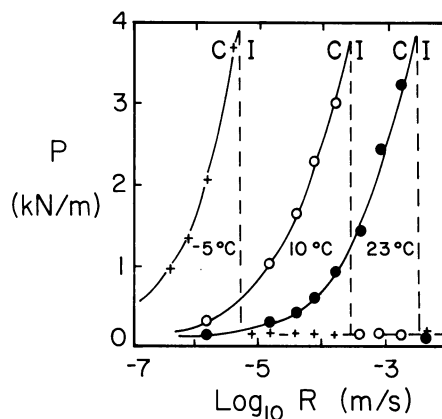


Fig. 34. Peel-force vs. rate of peeling for an elastomer layer adhering to Mylar. C and I denote cohesive and interfacial failure modes, respectively. (Taken from Ref. 168, published by Soc. Francaise de Chimie.)

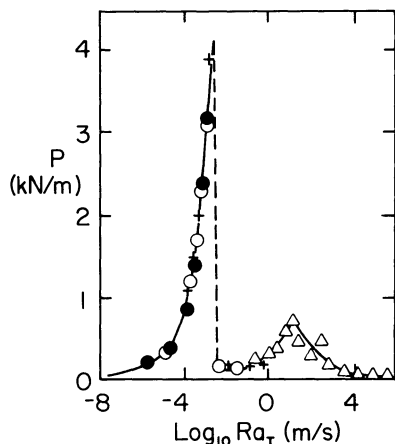


Fig. 35. Results from Fig. 34 replotted against the effective rate of peeling at 23°C. (Taken from Ref. 168, published by Soc. Francaise de Chimie.)

extending a viscous or viscoelastic liquid to the point of rupture.

These features of soft adhesives can be altered by changes in mix formulation. For example, the viscosity of the liquid can be adjusted by plasticization. The rate of deformation and temperature at which entanglements cease to slip free depend upon the molecular weight and glass transition temperature of the polymer. Thus, increasing the molecular weight, and increasing the glass temperature  $T_g$ , will lead to a reduction in the critical rate. Technically, it is advantageous to use carefully selected molecular weight distributions, incorporating a high molecular weight fraction, to add tackifiers and other adhesion-promoting additives, and vacuole initiators, such as poorly wetted particles, in order to maximize adhesion.

But it must be emphasized that a finite level of intrinsic, threshold, adhesion is necessary in order to take advantage of these various strengthening mechanisms. If there is no intrinsic adhesion, then there is no possibility of generating the deformations and dissipative processes at the interface that so greatly enhance the intrinsic strength.

### Autohesion

For similar layers to adhere well after being brought into contact, they must satisfy the basic criteria outlined previously. The two surfaces

must come into intimate molecular contact and the materials themselves must be able to resist high stresses without flowing apart. This latter property, denoted *green strength* is an important, but little understood, feature of elastomeric compounds. It distinguishes a strongly adhering elastomer from a simple liquid. Both may attain molecular contact readily, but, whereas liquids flow apart easily at low stresses, suitable elastomeric formulations will undergo large tensile deformations before rupturing. Amorphous elastomers (incapable of crystallizing upon stretching) rely on molecular entanglements to provide cohesion and green strength. When the molecular weight of these elastomers is less than the characteristic value at which entanglements form, then their green strength is low. On the other hand, when the molecular weight is much greater than the entanglement molecular weight, then they cease to flow like liquids and do not readily wet on contact.

A strain-crystallizing material like NR shows much better autohesion. It can be processed to a relatively low viscosity for easy wetting on contact, and still exhibit green strength due to strain-induced crystallization. Several other strain-crystallizable elastomers have been synthesized<sup>169,170</sup> and shown to exhibit autohesion and green strength comparable or superior to that of NR. These include: *trans*-polypentenamer, *trans*-butadiene-piperylene elastomers, and uranium-catalyzed polybutadiene.

Although crystallization on stretching is advantageous, it is quite undesirable for an elastomer to be partially crystalline in the unstrained state. This would seriously inhibit wetting and bond formation on contact. In this regard, partially crystalline EPR and EPDM have been reported to show very poor autohesion.<sup>171</sup>

**Interdiffusion.** When two identical layers are brought into contact, molecules from each surface may diffuse across the interface. This process is hastened when the molecular weight is low. It has been proposed<sup>172</sup> as a necessary condition for strong autohesion, whereas others<sup>173</sup> consider that intimate molecular contact at the interface is sufficient to give good

adhesion and that molecular diffusion across the interface is not really necessary. Pressure-sensitive adhesives certainly adhere strongly to substrates, such as glass, that are quite impermeable to polymer molecules.

Several investigators have examined the effect of contact time and pressure on autohesion.<sup>174-176</sup> In general, the strength of the bond increases to a plateau value after a sufficient time, Fig. 36.<sup>176</sup> When the plateau is reached, it is assumed that complete contact and interdiffusion have occurred. Fig. 37 shows self-diffusion coefficients  $D$  measured at room temperature for various elastomers as a function of molecular weight.<sup>177</sup> Although the data are limited, the points fall approximately on a single line, suggesting that the self-diffusion rates of NR and SBR are similar for a given molecular weight. For typical commercial elastomers, of molecular weight 200–300 K,  $D \approx 10^{-17} \text{ m}^2/\text{sec}$ . With this value of  $D$ , Skewis<sup>177</sup> estimated that one second after contact is achieved, a typical elastomer molecule would diffuse about 4.5 nm—enough for substantial interpenetration. Thus, for elastomers it appears that the development of good autohesion (tack) is limited principally by the difficulty in achieving good contact. This is further confirmed in a recent study.<sup>178</sup> When two rubber surfaces were brought together under a constant pressure at  $t = 0$ , and the pressure was

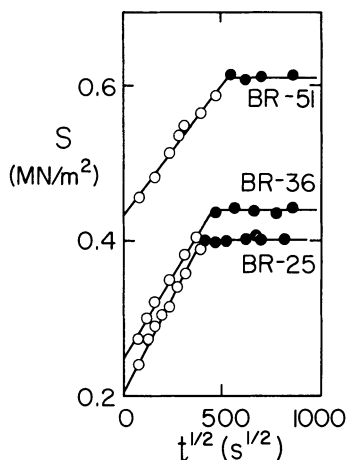


Fig. 36. Development of tensile strength  $S$  of autohesion with time  $t$  of contact for different types of polybutadiene. (Taken from Ref. 176, published by Rubber Division, American Chemical Society.)

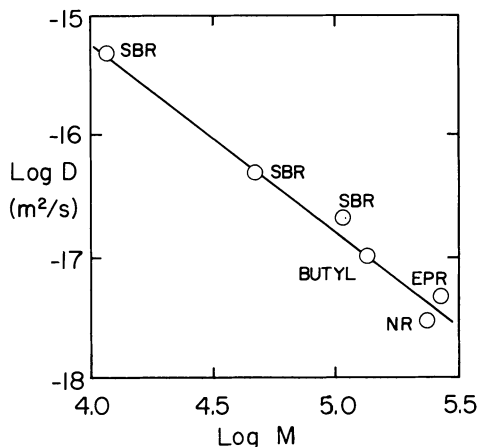


Fig. 37. Self-diffusion coefficients  $D$  of various elastomers as a function of molecular weight  $M$ . (Taken from Ref. 177, published by Rubber Division, American Chemical Society.)

later removed at  $t = t_1$ , the level of tack increased during the interval  $0 < t < t_1$ , but remained constant for  $t > t_1$ . Since interdiffusion is not a function of pressure, and would have continued after the pressure had been removed, this observation indicates that the extent of contact was the controlling factor.

**Effect of Molecular Weight.** The effect of polymer molecular weight on autohesion and strength is shown in Fig. 38 for NR.<sup>179</sup> As the molecular weight is increased the cohesive strength rises. On the other hand, the level of autohesion achieved after a given period in

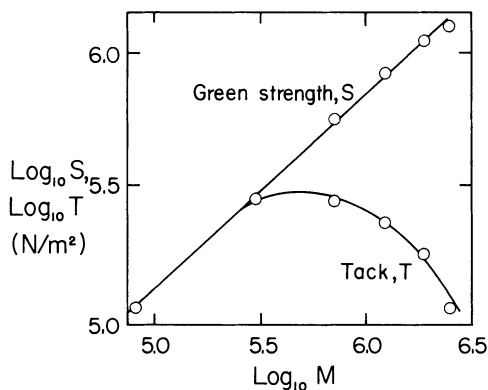


Fig. 38. Tensile strengths of autohesion (tack  $T$ ) and cohesion (green strength  $S$ ) as a function of molecular weight  $M$ . (Data taken from Ref. 179.)

contact passes through a broad maximum with increasing molecular weight.

At sufficiently low molecular weights, contact and diffusion are relatively rapid, but tack is low because of poor cohesive strength (*green strength limited*). At high molecular weights, both contact and diffusion are slow due to restricted molecular mobility, even though there is a substantial increase in green strength. Hence the relative tack is much less than unity and the absolute level of tack is low (*bond formation limited*). At intermediate molecular weights tack is maximized.

From a practical viewpoint, it is fortunate that the relationship between tack and molecular weight shows a rather broad maximum. This allows considerable variation in processing without great loss of green strength or tack.

## CONCLUDING REMARKS

Although major advances have been made in our understanding of surfaces, interfaces, bonding, and the strength of adhesive joints, as described in this chapter, there are still serious gaps. For example, there is a clear need for further application of fracture mechanics to adhesive joints. Tests in some geometrical arrangements cannot be used to predict fracture behavior in others, and this has led to broad dissatisfaction with present test methods. A wider application of the principles of fracture mechanics will eventually solve this particular problem, but it may also require the replacement of current test methods by others that are more directly relevant and more readily analyzed. For example, there does not appear to be at present a satisfactory method of measuring the strength of adhesion of thin films in terms of fundamental parameters.

Detailed stress analysis, including finite element techniques, should be carried out for increasingly complex model systems. Treatments need to be developed that properly take into account nonlinear, plastic, and viscoelastic response of both polymeric adhesives and bonded structural members. Indeed, recognition and understanding of the importance of energy dissipation within adhesives and adherends is essential in order to interpret much of the basic research in adhesion science. Many authors

have erroneously drawn conclusions about the intrinsic strength of interfacial bonds from mechanical tests in which the role of energy dissipation within the materials was not included.

## Durability

Adhesive bonds are degraded by various chemical reactions, notably hydrolysis, corrosion, and dissolution at the interface. Although primers and inhibitors minimize these effects, their role is not well understood. It is obvious that any systematic improvement in our present ability to forecast the service life of bonds will require a greater understanding of the processes involved in bond deterioration.

## Nondestructive Evaluation of Bonds

Perhaps the most serious need at the present time is for a method to assess the strength of an adhesive bond without actually breaking it. Methods exist for detecting defects at the interface, where the materials are not in contact, and this is an important part of nondestructive testing. But, as far as the authors are aware, there is no currently available method for assessing by nondestructive means whether a given bond is weaker than it should be.

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# Surface Preparation for Adhesive Bonding

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## INTRODUCTION

Adhesive bonding is unique among structural fabrication methods in having surface and interface properties so dominant in controlling bond formation and bond performance properties. A single molecular layer of contaminant can prevent proper wetting by the adhesive, or a weak substrate boundary layer can provide the “weak link” for premature failure. For these reasons, much adhesive application effort and technical study has been focused on the adhesive-substrate interface. With metals, surface characteristics are largely determined by the nearly always present oxide layer; this layer must be strongly adhering and resistant to humidity, etc., or it must be removed or specifically replaced by a more controlled oxide surface. With polymeric surfaces, successful bonding requires removal of contaminants, such as mold release residues, etc. In some cases, weak, low molecular weight fragments, which can be pushed to the polymer surface during crystallization processes, etc., must be removed.

In most practical cases involving metal surfaces, adhesive-substrate energetics are sufficient to cause wetting and adhesion. With many polymers, however, proper wetting and adhe-

sion to give reasonable strengths does not occur unless surfaces are increased in polarity by oxidation, plasma treatments, etc.

Over the past several decades, much study has been focused on surface energetics, wetting, adhesion, etc., and some generalizations have been developed. These can be useful guides to the adhesive selection and surface preparation needed to form reliable, strong adhesive bonds. Only a brief exposure to some of this valuable information can be presented here, but further reading is available in Chapter 3 and other chapters of this Handbook, and in listed references.

## TECHNICAL BACKGROUND

Many intermolecular material properties, including volatility and heat of vaporization, surface tension, viscosity, solubility relationships, etc. are determined by secondary valence forces.<sup>1</sup> These same secondary valence forces are mainly responsible for critical adhesive bond needs, such as wetting and adhesion. These forces include: (1) London or dispersion forces, the net charge separation or dipoles resulting from the instantaneous imbalance of electrons in their orbits, which are relatively weak and short range but present in all mate-

rials; (2) dipole-dipole forces due to the charge imbalance in certain covalent bonds because of the presence of electronegative or electropositive elements; and (3) hydrogen bonds, a special class of relatively energetic dipole-dipole interaction, due to the presence of hydrogen bond donor and acceptor groups. Examples of such bonds are shown in Table 1.

To be effective in promoting interaction between materials (solvency, wetting, adhesion, etc.), specific matched secondary forces must be present in both materials or they will prefer interacting with their own molecules. For example, alcohols, with strong hydrogen bonds, will not dissolve in a hydrocarbon which has only dispersion forces at work. Also, an epoxide adhesive, with strong dipoles and hydrogen bonding groups, will meet its energy sharing needs internally and not wet a polyethylene or polypropylene surface where it can only share the weak dispersion forces that are present in common. Oxidation or plasma treatment of such a low energy polyethylene surface, generating dipolar or hydrogen bonding groups, now allows such interacting to occur. Such treated surfaces can now be bonded with polar epoxide adhesives.

Several methods of quantitatively measuring the relative energy of materials, both liquids and solid surfaces, have been developed and can be of major help in predicting wetting characteristics or surface modifications needed for effective adhesive bonding.

### Solubility Parameter<sup>2</sup>

Based, for liquids, on the heat of evaporation (the energy needed to separate the molecules from each other), this reflects the relative co-

hesive energy density which results from the interaction of the secondary valence forces present. Summaries of such values for a broad range of monomeric and polymeric materials are found in a number of books and articles.<sup>2,3</sup> Values for polymers are deduced indirectly from their solubility or swelling in selected solvents. Often single numbers are given, but by far the most useful information contains the separate energy components due to dispersive, polar and hydrogen bonds. Typical values are shown in Table 2. Such information can predict, directly, solubility and compatibility relationships, and indirectly, indicate surface energy and wetting potentials.

### Contact Angle Measurements

The angle at the edge of a drop of liquid applied to a solid surface reflects the ability of the secondary valence forces of the liquid to interact with those on the solid surface. This situation, shown in Fig. 1, has been developed by Young<sup>4</sup> into an equation describing the balance of interfacial forces or surface tensions or energies ( $\gamma$  = surface tensions at solid-vapor, solid-liquid, and liquid-vapor interfaces):

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta$$

A low liquid contact angle indicates a good affinity and a good potential for wetting of the solid.

A further extension of these energy relationships, the Young-Dupré equation,<sup>5</sup>  $W_a = \gamma_{LV} (1 + \cos \phi)$ , relates the work of adhesion, or bonding energy, directly to the surface tension of the liquid and the contact angle that the liquid makes with the solid.

**Table 1. Intermolecular Forces.**

Type	Examples	Relative Strength
London dispersion	Transient displaced electrons	Weak, but present in all materials
Dipole-dipole	H-F, -C-Cl, -C≡N, =C=O	Medium
Hydrogen bonds	Donors: -O-H, -N-H	Strong
	Acceptors: O=C=, O / H \ R	

**Table 2. Critical Surface Tensions and Solubility Parameters of Polymeric Solids.<sup>2</sup>**

<i>Polymer</i>	$\gamma_c$ , dynes/cm	<i>Solubility parameter, (cal/cm<sup>3</sup>)<sup>1/2</sup></i>
Polyhexafluoropropylene	16	6
Polyvinyl fluoride	28	—
Polyethylene	31	8
Polystyrene	33	8.6–9.1
Polyvinyl alcohol	37	—
Polyvinyl chloride	39	9.6
Polyethylene terephthalate	43	10.7
Polyhexamethylene adipamide	46	13.6
Metals	> 500	—

**Critical Surface Tension of Solid**

Although the surface tension of solids cannot be measured directly, an empirical method developed by Zisman<sup>6</sup> has allowed a very useful relative surface energy value to be obtained. This can be done by measuring the contact angle (Fig. 1) made by a homologous series of pure liquids, of known surface tensions, with a solid surface, and plotting the results as in Fig. 2. Extrapolating to a zero contact angle ( $\cos \theta = 1$ ) and extending the intercept to the surface tension axis gives the *critical surface tension* of the solid surface. An extension of this work by Kaelble,<sup>7</sup> taking into account the special influence that polar and especially hydrogen bonding forces can have on such liquid-solid interactions, has made such determinations even more useful.

These relationships can be of high predictive value and indicate that good wetting of a solid

surface will occur if the critical surface tension is higher than the surface tension of the applied adhesive. (Viscosity, time, etc. are also important variables.) Typical values of high and low energy surfaces are included in Table 2.

**Examples of Surface Energy Relationships**

Consideration of all the above energy relationships and derived values can be of great help in selecting adhesives and surface preparation conditions for attaining predictable, strong adhesive bonds. Several examples are presented here.

In the bonding of a polyester substrate (solubility parameter 10.3) with a series of adhesives<sup>8</sup> having solubility parameters ranging from 8 up to 13, measured peel strengths were greatly increased as the solubility parameter of the selected adhesive neared a match with that of the substrate (Fig. 3). When so matched, the potential for interdiffusion would be maximized and the failure location was directed away from the interface.

From Tables 2 and 3, an epoxide adhesive (surface tension 45 dynes/cm) would not be expected to wet and effectively bond a low energy surface such as polyethylene (critical surface tension 31 dynes/cm). When the polyethylene surface was etched for increasing times in a sulfuric acid-dichromate solution, bond strengths markedly increased and the surface's contact angle with water (increasing polarity) similarly decreased (Fig. 4).<sup>9</sup>

$$\gamma_{SV} - \gamma_{SL} = \gamma_L \cos \theta$$

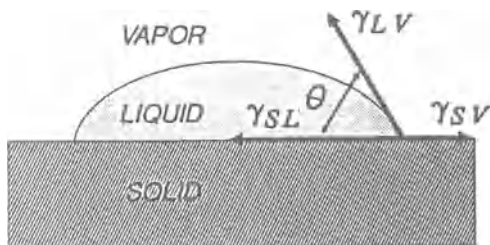


Fig. 1. Contact angle.

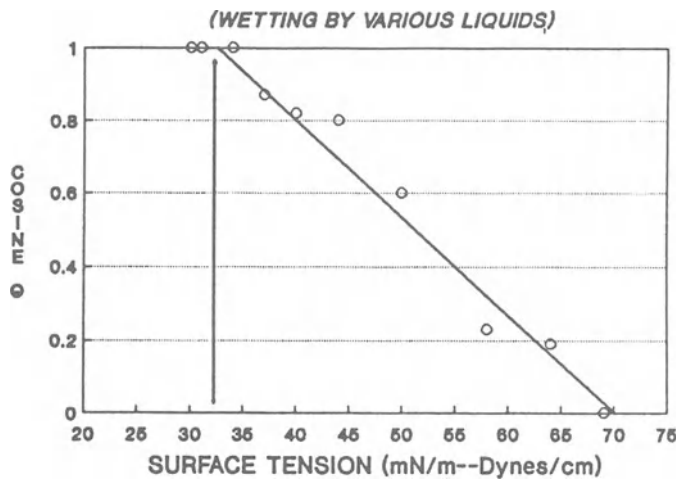


Fig. 2. Determination of critical surface tension of solid surfaces.

**SURFACE PREPARATION**

**General Considerations**

[Based on Dexter Adhesives and Structural Materials Division, The Dexter Corporation, Bulletin G1-600 and indicated referenced sources. See also ASTM D2651-79,

“Standard Recommended Practice for Preparation of Metal Surfaces for Adhesive Bonding” for general procedures.]

To correctly prepare the surface to be joined, all grease, oil, and foreign particles should be removed. With most high performance adhesives this step is critical, since for good wet-

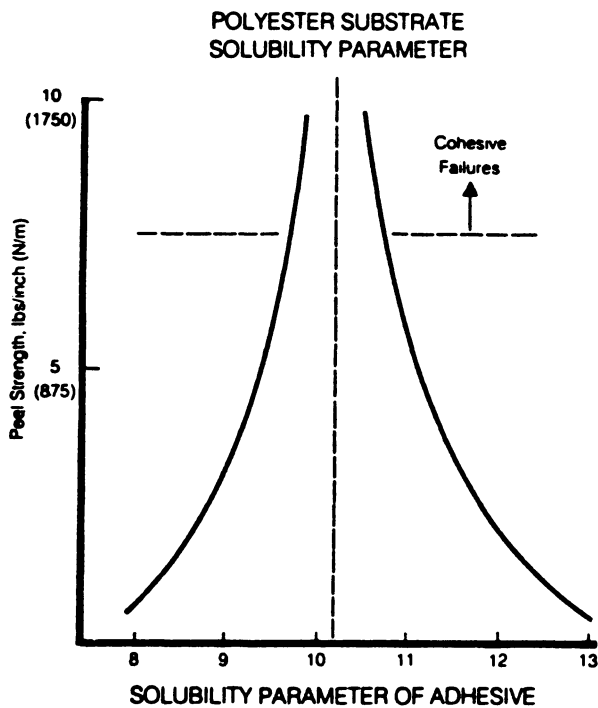


Fig. 3. Peel strength of polyester substrate bonded with various adhesives.



**Table 3. Liquid Surface Tension and Solubility Parameter Correlation with Structure.**

Material	Intermolecular Forces	Surface Tension dynes/cm	Solubility Parameter, (cal/cm <sup>3</sup> ) <sup>1/2</sup>			
			Total <sup>a</sup>	Dispersion	Polar	Hydrogen Bond
<i>n</i> -Hexane	Dispersion only	18.4	7.24	7.23	0.0	0.0
Methylene chloride	Dispersion plus dipole-dipole	26.5	9.93	8.91	3.1	3.0
Methanol	Dispersion plus hydrogen bond	22.6	14.3	7.4	6.0	10.9
Water	Dispersion plus hydrogen bond	73	23.5	6.0	15.3	16.7
Typical epoxide adhesive	Dispersion plus hydrogen bond	45	8-13	(moderate H bonding)		

$$^a\text{Total} = \sqrt{d^2 + p^2 + h^2}$$

ting, the adherend should have a higher surface tension than the adhesive. Even a thumbprint on an otherwise clean surface can prevent the adhesive from spontaneously wetting and spreading.

Organic contaminants are removed by degreasing, while loose deposits are dislodged by scraping or washing with acids, alkali solutions, or other such chemicals. Metals are best cleaned by vapor degreasing with trichloro-

ethane, followed by sandblasting or, preferably, by chemical etching. Chemical treatments may be confined to the bonding areas, but degreasing should be done to the entire assembly. A cleaned assembly should be bonded as soon after the cleaning operation as possible, or an adhesive primer should be applied. However, if storage is necessary, special precautions should be taken so that the assembly does not become contaminated. All parts should be

### EPOXY RESIN--POLYETHYLENE JOINT STRENGTH (CHROMIC ACID SURFACE TREATMENT)

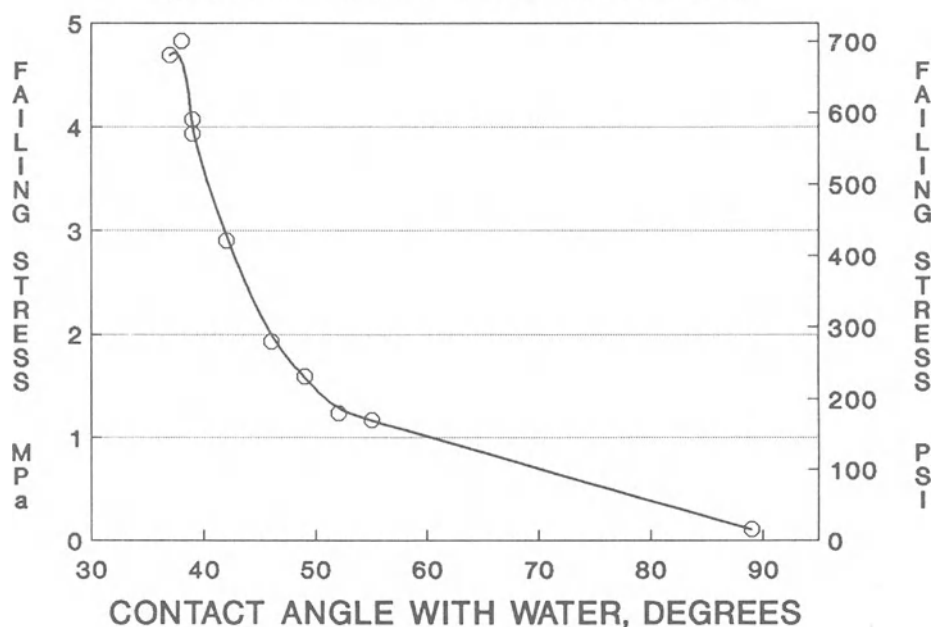


Fig. 4. Bond strengths between epoxide resin and surface-treated polyethylene.

tightly wrapped or placed in airtight and oil-free containers. Etched surfaces must never be touched with bare hands—even wiping the surface with a clean cloth can affect the bond. Handlers should wear clean cotton gloves and use clean tools.

Nonmetallic, nonporous materials should be degreased with a detergent solution, rinsed thoroughly with clean water, and then dried. Clean solvent may be substituted for detergent. The surfaces are then hand-sanded or sand-blasted to give them a rough texture.

Water is often used to test a metal surface for cleanliness. A small portion is placed on the surface. If the water distributes evenly, then the metal should wet well with an adhesive. But if it beads or crawls, then the surface should be cleaned again and the test repeated.

Bonding should be performed in a room separate from other manufacturing operations. When bonding is done in the same area as plastic or rubber molding, a physical barrier should be erected between the two operations to prevent airborne mold lubricants from depositing on the metal. Similar hazards are presented by spray painting, electroplating, etching, and machining with coolants. Storage and assembly areas should be enclosed, and air to these areas filtered and under slight pressure.

Numerous studies are underway to find surface treatment methods that minimize or eliminate use of toxic materials or polluting substances. Some progress is being made,<sup>13,14</sup> but replacement of such degreasing solvents as trichloroethane and such toxic materials as the dichromates will take time. For polymeric surfaces, plasma or corona discharge treatments are receiving much attention.

### Degreasing Metals

To degrease metal surfaces with a degreasing unit, suspend the metals in a stabilized trichloroethane vapor bath for about 30 seconds. Check the bath frequently for accumulated contaminants. If a degreasing unit is not available, clean the surface with a white cotton rag or pieces of absorbent cotton dampened in trichloroethane. Rags should be changed frequently. Let the surface stand several minutes while the chemical evaporates. Although non-

flammable, this solvent is toxic in both liquid and vapor forms, so the working area should be well ventilated. Gloves should be worn when handling this solvent, and smoking should not be allowed.

### Degreasing Nonmetals

Solvents or detergent solutions can be used to remove mold-release agents or waxes from plastics. Commercial detergents such as Sprex (DuBois Chemical Co., 1120 West Front, Cincinnati, Ohio) are suitable. Acetone and methyl alcohol are effective solvents, depending on the type of plastic to be cleaned. The adverse effect of solvents on some polymeric materials should be checked before their use.

### Surface Abrasion

Smooth surfaces can be improved for bonding by roughening with abrasives such as medium grit emery paper. Abrasion should always be followed by degreasing to remove contaminants and loose particles.

Blasting with a fine grit is the best method for removing surface deposits—oxide films, tarnish, rust, mill scale, and other contaminants—from metals. This method should be used only on structures thick enough to resist distortion. With thinner materials, contaminants should be removed by vapor honing. This method is similar to grit blasting but uses high-velocity water or steam instead of air. If neither method is appropriate, abrasive disks, belts, cloth, medium-grit emery paper, or wire brushes can be used. Plastics should be roughened with abrasive disks, belts, cloth, or emery paper to remove mold release agents. Medium-grit emery paper will give the best results.

Surface abrasion can also remove other surface contaminants as well as weak, low molecular weight components which can be concentrated at the surface due to their exclusion during solidification or crystallization of some polymers.<sup>10</sup> Also, during solidification of both thermoplastic and thermoset materials there is often an orientation of the more polar groups toward the interior, leaving a concentration of lower polarity, lower energy groups on the surface.<sup>11</sup> Abrasion can open up access to the more energetic polymer interior.

### Chemical Treatment

Chemical or electrolytic pretreatments of a bonding surface can greatly increase the strength of the bond. Pretreating can etch the surface of a metal, and form a highly adherent oxide. Environmental resistance can often be greatly increased by such treatment. Etching solutions should be prepared in glass, porcelain, polyethylene, polypropylene, or tetrafluoroethylene fluorocarbon laboratory ware and stirred with rods of the same material. Metals other than those to be etched should not touch the solutions. For solutions containing hydrofluoric acid or fluorides, TFE fluorocarbon should be used. Solutions in plastic trays can be heated by immersion in hot water baths; hot plates or infrared heaters can be used for glass and porcelain trays. See Caution section below for safe procedures.

### Caution

The Occupational Safety and Health Administration of the Department of Labor has defined some of the following chemicals and substrates to be hazardous to health in varying degrees. Some are even extremely hazardous. You should familiarize yourself with the substrates and needed chemicals and know the safe handling procedures to be used before preparing the surfaces for adhesive bonding. Also, many of the solvents, degreasing solvents and etch bath chemicals are toxic or can be dangerous if not mixed and handled properly. Materials such as hydrofluoric acid and the chromates need very careful handling. Care should be taken in preparing such chemical solutions, not only because the wrong proportions can seriously weaken a bond but also because the chemicals can be harmful to the skin. Many are strong acids and bases. Remember that solutions containing concentrated sulfuric acid must be prepared by adding acid to water with stirring, and not vice versa. A violent reaction can occur if this is not observed. Use rubber gloves, aprons, face shields, etc.

While the information contained in this article is believed to be reliable, surface treating methods have been selected from many sources, substrates can vary considerably from

source to source, and bonding conditions can vary with location and the experience of the operator. Therefore, all recommendations are made without guarantee and those following such listed procedures should become familiar with the general requirements of adhesive bonding and run controls with specific materials and processes before proceeding with the preparation of critical bonded structures.

### Surface Treatment Tables

The following tables on surface treatment for bonding use are based largely on data from Dexter Bulletin G1-600 and indicated references. A number of abbreviations have been used to reduce their length. These include the following: Parts by weight—pbw; distilled or deionized water—DI water; minutes—min; hours—hr; chemical names—chemical symbols, i.e., hydrofluoric acid—HF, hydrochloric acid—HCl, sulfuric acid—H<sub>2</sub>SO<sub>4</sub>, sodium dichromate—Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, sodium hydroxide—NaOH, etc.

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## Surface Treatment—Metals.

<i>Adherent Material</i>	<i>Cleaning</i>	<i>Abrasion or Chemical Treatment</i>	<i>Method</i>
Aluminum and alloys	Degrease in vapor bath of trichloroethane. (See ASTM D2651 for general information. See Ref. 12 for chromate-free P2 etch.)	<p>(A) Chromic acid etch: DI water <math>\text{H}_2\text{SO}_4</math> (conc.) <math>\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}</math> 2024 bare aluminum Dissolve the 20 mil aluminum sheet to "seed" the bath.</p> <p>(B) Phosphoric acid anodizing (Boeing Co. patent appl.) (for improved environmental resistance) (ASTM D3933-80): Prepare anodizing bath: <math>\text{H}_3\text{PO}_4</math> (75% conc.) DI water Add acid to water with stirring. Use titanium racks and a stainless steel cathode.</p>	<p>(A)</p> <ul style="list-style-type: none"> <li>Etch metal in bath for 12–15 min at 150–160°F (66–71°C).</li> <li>Do not delay rinse! Spray in tap water for 5 min.</li> <li>Follow with DI water soak rinse.</li> <li>Dry thoroughly at 120–140°F max. (49–60°C).</li> <li>Do not touch bonding surface.</li> <li>Prime or bond within 16 hr.</li> </ul> <p>(B)</p> <ul style="list-style-type: none"> <li>Prepare etched metal as above in (A).</li> <li>Anodize at 65–85°F (18–30°C).</li> <li>Slowly raise voltage to 10–11 V for 20–25 min.</li> <li>Disconnect current, immediately remove parts and rinse in running water (DI or &lt;150 ppm solids tapwater) for 10–15 min.</li> <li>Dry at 160°F (71°C) max.</li> <li>Do not touch surface.</li> <li>Prime or bond within 16 hr.</li> </ul>
Aluminum honeycomb core	Degrease in vapor bath of trichloroethane.	Not used.	<ul style="list-style-type: none"> <li>After degreasing, let stand 2 hr at room temp or 15 min at 200°F (93°C).</li> </ul>
Beryllium (highly toxic)	Degrease in vapor bath of trichloroethane.	Dissolve NaOH in equal weight of DI water, then add water to reduce concentration to 20% w.	<ul style="list-style-type: none"> <li>Immerse in conc. (20% w) NaOH soln. 3 min at 180°F (82°C).</li> <li>Rinse thoroughly in cold running DI water.</li> <li>Finally, dry in oven for 10–15 min at 300–350°F (149–177°C).</li> </ul>
Cadmium	Degrease.	Abrade with emery paper. Preferably electroplate with silver or nickel for bonding.	<ul style="list-style-type: none"> <li>Repeat degreasing step.</li> </ul>

(Continued on page 82)

Surface Treatment — Metals (*Continued*).

<i>Adherend Material</i>	<i>Cleaning</i>	<i>Abrasion or Chemical Treatment</i>	<i>Method</i>
Copper and alloys brass, bronze	Degrease in vapor bath of trichloroethane. (Also see Ref. 12 and ASTM D2651-79.)	(A) For medium strength bonds, abrade with emery paper. (B) <i>For high bond strengths etch metal surface in:</i> 42% Aqueous FeCl <sub>2</sub> soln. 15 pbw Conc. HNO <sub>3</sub> (s.g. 1.41) 30 pbw DI water 197 pbw	(A) • Repeat degreasing step. (B) • Immerse for 1-2 min at 77°F (25°C). • Rinse in cold running DI water. • Dry immediately with pressurized air at room temp. (77°F, 25°C).
Gold	Degrease with vapor bath or clean rag and solvent.	None.	• Degreasing only treatment.
Iron: Cast iron (alloys under steel)	Degrease in vapor bath of trichloroethane.	Grit blast or abrade with emery paper.	• Repeat degreasing step.
Lead and alloys, pewter	Degrease in vapor bath of trichloroethane.	Abrade with medium grit emery paper.	• Repeat degreasing step.
Magnesium and alloys	Wash with liquid trichloroethane, then— <i>Caution</i> —30 seconds only in trichloroethane vapor bath. (See ASTM D2651-79.)	(A) For medium strength bond, abrade with medium-grit emery paper. (B) For high strength bonds, use etch procedure. (ASTM D2651, Method A) <i>Bath 1:</i> Sodium metasilicate 2.5 pbw Tetrasodium pyrophosphate 1.1 pbw Sodium hydroxide 1.1 pbw Nacconol® NR (Allied Chem. Corp.) 0.3 pbw DI water 95 pbw <i>Bath 2:</i> Chromium trioxide 1 pbw DI water 4 pbw	(A) • Repeat degreasing step. • Dry in forced draft oven at 150-200°F (66-93°C). (B) • Immerse metal for 10 min in Bath 1 at 140-160°F (60-71°C). • Rinse thoroughly in water. • Immerse metal for 10 min in Bath 2 kept at 140-190°F (71-88°C). • Wash in cold running DI water. • Dry in a forced-draft oven at <140°F (60°C). • When cool, immediately apply adhesive.

Nickel	Degrease.	(A) For medium strength bond, abrade with medium-grit emery paper. (B) For higher bond strengths, conc. HNO <sub>3</sub> (s.g. 1.41), <sup>12</sup>	(A) • Repeat degreasing step. (B) • For stronger bond, immerse metal for 5 seconds in conc. HNO <sub>3</sub> solution at room temp. (77°F, 25°C). • Rinse etched metal thoroughly in cold running DI water. • Air dry at 104°F (40°C).
Platinum	Degrease.	No other treatment needed.	
Silver	Degrease.	Using fine-grit emery paper, remove any tarnish from bonding area.	• Repeat degreasing step.
Steel and iron alloys (except stainless steel)	Degrease in vapor bath of trichloroethane.	(A) Sandblast or abrade with medium-grit emery paper. (B) If cannot sandblast or abrade: <i>Acid Bath 1:</i> Conc. orthophosphoric acid (s.g. 1.73) Ethyl alcohol (denatured) or <i>Acid Bath 2:</i> Conc. HCl DI water	(A) • Repeat degreasing step. (B) • Immerse for 10 min in Acid Bath 1 at 140°F (60°C) or 5–10 min in Bath 2 at 68°F (20°C). • Remove black residue with stiff brush under running DI water. • Dry at 250°F for 1 hour. If cannot be stored at less than 30% Relative Humidity, bond prepared surfaces in short time.
Steel, ferrous alloys	Degrease in vapor	(A) Gritblast if possible. (B) If cannot abrade: Conc. HCl DI water	(A) • Repeat degreasing step. (B) • If cannot abrade immerse for 3–10 min at 77°F (25°C) in HCl bath. • Rinse thoroughly in cold running DI water. • Oven dry at 150°F (66°C) for 10 min.

(Continued on page 84)

Surface Treatment—Metals (*Continued*).

<i>Adherent Material</i>	<i>Cleaning</i>	<i>Abrasion or Chemical Treatment</i>	<i>Method</i>
Stainless steel	Degrease by washing in trichloroethane. (See Ref. 14 for alternate procedures. Also see ASTM D2651.)	Remove surface deposits with nonmetallic agent— alumina grit paper. (A) General Purpose Treatment: <i>Bath 1:</i> See under Magnesium and alloys.  (B) For high temperature use, further treat the metal: <sup>1,2</sup> <i>Bath 2:</i> Oxalic acid Conc. H <sub>2</sub> SO <sub>4</sub> (s.g. 1.86) DI water  Dissolve oxalic acid before stirring in the H <sub>2</sub> SO <sub>4</sub> .  <i>Bath 3:</i> Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O DI water Conc. H <sub>2</sub> SO <sub>4</sub> (s.g. 1.86)	(A) <ul style="list-style-type: none"> <li>Immerse in Bath 1 for 10 min. at 160–180°F (71–82°C).</li> <li>Rinse thoroughly in running tapwater then cold DI water.</li> <li>Oven dry at 200°F (93°C) for 10 min.</li> <li>Bond as soon as possible.</li> </ul> (B) <ul style="list-style-type: none"> <li>Immerse metal for 10 min in Bath 2 at 185–195°F (85–90°C).</li> <li>Under cold running water, scrub away any black residue with clean, stiff bristle brush.</li> <li>Rinse in DI water.</li> <li>Dry in oven at 200°F (93°C) for 10–15 min.</li> </ul> (C) <ul style="list-style-type: none"> <li>Immerse in Bath 3 at 140–160°F (60–71°C) for 15 min.</li> <li>Scrub under cold running water with stiff bristle brush.</li> <li>Rinse in DI water.</li> <li>Dry in oven at 200°F (93°C) for 10–15 min.</li> </ul>
Tungsten and alloys	Degrease in vapor bath of trichloroethane.	(A) Abrade using medium-grit emery paper. (B) For maximum strength, also use a chemical etch:  Conc. HCl DI water HF Conc. H <sub>2</sub> SO <sub>4</sub> Hydrogen peroxide  Add HCl and HF to the water, stir in the H <sub>2</sub> SO <sub>4</sub> then add the hydrogen peroxide.  Abrade with medium-grit emery paper.	(A) <ul style="list-style-type: none"> <li>Repeat degreasing step.</li> </ul> (B) <ul style="list-style-type: none"> <li>Immerse for 1–5 min at 77°F (25°C).</li> <li>Rinse thoroughly in cold, running DI water.</li> <li>Dry for 10–15 min in a 160–180°F (71–82°C) oven.</li> </ul>
Tin	Degrease.		<ul style="list-style-type: none"> <li>Repeat degreasing.</li> </ul>

Titanium and alloys (Many procedures in literature. Also see ASTM D2651.)	Vapor degrease with trichloroethane. Remove surface deposits with nonmetallic abrasive.	<p>(A) <i>Bath 1:</i> Sodium metasilicate soln. (see Magnesium).</p> <p>(B) For stronger bonds:</p> <p><i>Bath 2 (polyethylene vessel):</i> Sodium fluoride 10 pbw Chromium trioxide 5 pbw DI water 250 pbw Conc. <math>H_2SO_4</math> (add last with stirring) 50 pbw</p>	<p>(A)</p> <ul style="list-style-type: none"> <li>Immerse at 160–180°F (71–82°C) for 10 min.</li> <li>Rinse in cold, running DI water.</li> <li>Dry in oven at 150–200°F (66–93°C) for 10–15 min.</li> </ul> <p>(B)</p> <ul style="list-style-type: none"> <li>Immerse in Bath 2 at room temp. for 5–10 min.</li> <li>Rinse in cold, running DI water.</li> <li>Dry in oven at 160–180°F (71–82°C) for 10–15 min.</li> </ul>
(C)	Alternate Treatment (ASTM D2651):	<p><i>Bath 3 (alkaline-clean):</i> Oakite HD 126 1.5 oz DI water to 1 gal</p> <p><i>Bath 4 (acid pickle):</i> HF (70%) 2–3 oz (fl) <math>Na_2SO_4</math> (anhyd.) 3.0 oz <math>HNO_3</math> (70%) 40–50 oz DI water to 1 gal</p> <p><i>Bath 5 (etch bath):</i> Trisodium phosphate 6.5–7 oz Potassium fluoride 2.5 oz HF (70%) 2.2–2.5 oz DI water to 1 gal</p>	<p>(C)</p> <ul style="list-style-type: none"> <li>Immerse in Bath 3 for 5 min at 150°F (66°C).</li> <li>Rinse in running tapwater at 105°F (40°C) for 2 min.</li> <li>Immerse in Bath 4 for 2 min at room temp.</li> <li>Rinse in cold water.</li> </ul> <ul style="list-style-type: none"> <li>Immerse in Bath 5 for 2 min at room temp.</li> <li>Rinse in DI water at 150°F (66°C) for 15 min.</li> <li>Repeat rinse.</li> <li>Dry at 140°F (60°C) for 30 min in air circulating oven.</li> <li>Wrap in clean kraft paper.</li> </ul>
Zinc, alloys, galvanized metals	Degrease in vapor bath of trichloroethane.	<p>(D) Surface treatments with Pasa Jell 107 can also be used (SemCo Div., PRC).</p> <p>(A) Abrade using medium-grit emery paper.</p> <p>(B) For maximum strength:</p> <p>Conc. HCl 20 pbw DI water 80 pbw</p>	<p>(A)</p> <ul style="list-style-type: none"> <li>Repeat degreasing step.</li> </ul> <p>(B)</p> <ul style="list-style-type: none"> <li>Immerse for 2–4 min with the solution at 77°F (25°C).</li> <li>Rinse thoroughly in cold, running DI water.</li> <li>Dry for 20–30 min. in a 150–160°F (66–71°C) oven.</li> <li>Apply adhesive as soon as possible.</li> </ul>



## Surface Treatment — Thermoplastics.

<i>Adherend Material</i>	<i>Cleaning</i>	<i>Abrasion or Chemical Treatment</i>	<i>Method</i>
ABS (Ref. 12)	Degrease in acetone. (Alcohols probably better to use.)	(A) Abrade with medium-grit sandpaper. (B) Etch solution: Conc. H <sub>2</sub> SO <sub>4</sub> K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> DI water (Add acid to stirred water)	(A) <ul style="list-style-type: none"> <li>• Wipe free of dust.</li> <li>• Prime with Dow Corning A-4094 or G.E. SS-4101.</li> </ul> (B) <ul style="list-style-type: none"> <li>• Etch at room temp. for 20 min.</li> <li>• Rinse in tapwater.</li> <li>• Rinse in DI water.</li> <li>• Dry in warm air.</li> </ul>
Cellulose plastics	Degrease with methyl alcohol or isopropyl alcohol.	Abrade using fine-grit emery paper or gritblast.	<ul style="list-style-type: none"> <li>• Repeat degreasing step.</li> <li>• Heat to 200°F (93°C) for 1 hr and apply adhesive while hot.</li> </ul>
Diallylphthalate Fluorocarbons: • Polymonochlorotrifluoroethylene • Polytetrafluoroethylene • Tetrafluoroethylene • Polyvinyl fluoride	Degrease with acetone or MEK. Degrease with acetone or MEK. Also see Ref. 12; flame treatment and corona discharge, etc., also used.	Abrade using medium-grit emery paper. Use chemical etch: Sodium metal Naphthalene Tetrahydrofuran  23 g 128 g 1 l  Prepare under anhydrous conditions (dry solvents, closed flask, stirrer, drying tube). Add naphthalene to the THF, carefully add 1/4-1/2" cubes of sodium, one at a time, while stirring. Let soln. stand 16 hr at room temp., then stir 2 hr. Store in bottles with glass stoppers; keep free from air and moisture. Use near exhaust ventilator.	<ul style="list-style-type: none"> <li>• Repeat degreasing step.</li> <li>• Immerse in the solution for 15 min at 77°F (25°C).</li> <li>• Wash in acetone or MEK then in cold, DI water.</li> <li>• Dry thoroughly.</li> <li>• Proprietary solutions may be used: Bondaid W.S. Shamband Co. Fluorobond Joclin Mfg. Co. Fluorotetch Acton Associates Tetraetch W.L. Gore Assoc.</li> </ul>

Nylon	Degrease with acetone or MEK.	Abrade using medium-grit emery paper.	<ul style="list-style-type: none"><li>• Repeat degreasing step.</li></ul>												
Polycarbonate, polymethylmethacrylate, or polystyrene	Degrease with methyl alcohol.	Abrade using medium-grit emery paper.	<ul style="list-style-type: none"><li>• Repeat degreasing step.</li></ul>												
Polyether (chlorinated), polyethylene, polypropylene, or polyformaldehyde	Degrease with acetone or MEK. See Ref. 13 for alternate procedures. Flame or plasma treatment may also be used (see Ref. 12).	<p>Chemical pretreatment is necessary:</p> <table><tr><td><math>K_2Cr_2O_7</math></td><td>75 pbw</td></tr><tr><td>DI water</td><td>120 pbw</td></tr><tr><td>Conc. <math>H_2SO_4</math></td><td>1500 pbw</td></tr></table> <p>Dissolve the <math>K_2Cr_2O_7</math> in water and stir in the <math>H_2SO_4</math>.</p>	$K_2Cr_2O_7$	75 pbw	DI water	120 pbw	Conc. $H_2SO_4$	1500 pbw	<p>(A)</p> <ul style="list-style-type: none"><li>• Immerse in the chromic acid solution as follows:<table><tr><td>Chlorinated polyether</td><td>5 min. at 160°F (71°C)</td></tr><tr><td>Polyethylene and polypropylene</td><td>60 min. at 77°F (25°C)</td></tr><tr><td>Polyformaldehyde</td><td>10 sec. at 77°F (25°C)</td></tr></table></li><li>• Rinse in cold, running DI water.</li><li>• Dry at room temp.</li></ul> <p>(B)</p> <ul style="list-style-type: none"><li>• Flame or plasma treatments may be used also.</li></ul>	Chlorinated polyether	5 min. at 160°F (71°C)	Polyethylene and polypropylene	60 min. at 77°F (25°C)	Polyformaldehyde	10 sec. at 77°F (25°C)
$K_2Cr_2O_7$	75 pbw														
DI water	120 pbw														
Conc. $H_2SO_4$	1500 pbw														
Chlorinated polyether	5 min. at 160°F (71°C)														
Polyethylene and polypropylene	60 min. at 77°F (25°C)														
Polyformaldehyde	10 sec. at 77°F (25°C)														
Polyethyleneterephthalate or linear polyesters	Degrease with methyl alcohol. See Ref. 12; plasma treatments also used.	<p>(A) Abrade using medium-grit emery paper.</p> <p>(B) For a stronger bond use chemical etch: Sodium hydroxide solution (20%w)</p>	<p>(A)</p> <ul style="list-style-type: none"><li>• Repeat degreasing step.</li></ul> <p>(B)</p> <ul style="list-style-type: none"><li>• Immerse for 2–10 min. at 160–200°F (71–93°C).</li><li>• Wash thoroughly in cold, running DI water.</li><li>• Dry with hot air.</li><li>• Repeat degreasing step.</li></ul>												
Polyvinylchloride, rigid	Degrease with methanol or trichloroethane.	Abrade using medium-grit emery paper.													

## Surface Treatment—Engineering Thermoplastics (Examples of Representative Commercial Materials).

<i>Adherend Material</i>	<i>Cleaning</i>	<i>Abrasion or Chemical Treatment</i>	<i>Method</i>
Polyarylate (Ardel <sup>®</sup> , U.C.) <sup>12</sup> or polyaryl sulfone (Astrel <sup>®</sup> 360, 3M) <sup>12</sup>	(A) Ultrasonic clean in alkaline-etching solution.	(A) Using alkaline-etching solution, sandblast with 150 mesh silica sand. (B) Acid etch solution: Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O Conc. H <sub>2</sub> SO <sub>4</sub> 3.4%W 96.6%W (C) Corona or Plasma treatment	(A) • Water wash. • Alcohol wash. • Dry with dry nitrogen. (B) • Immerse 15 min at 150–160°F (66–71°C) • Cold water wash. • Dry at 150°F (66°C) in an air circulating oven.
Polyether-ether-ketone (PEEK <sup>®</sup> , ICI) <sup>12</sup>	Degrease with trichloroethane or isopropyl alcohol.	(A) Abrade (B) Flame treatment: blue oxidizing flame. (C) Chromic acid etch (bath composition not given in Ref. 12). (D) Corona or Plasma treatment.	(A) • Repeat degrease. (B) • Abrade. • Degrease. • Flame treat (blue oxidizing flame). (C) • Abrade. • Degrease. • Chromic acid etch. • Water wash.
Polyphenylene sulfide Ryton <sup>®</sup> , Phillips) <sup>12</sup>	(A) Degrease with acetone. (B) Wipe surface with ethyl alcohol soaked paper.	(A) Sandblast. (B) Sand with 120-grit sandpaper. (C) Corona or plasma treatment.	(A) • Repeat degreasing. (B) • Clean off dust with stiff bristled brush.
Polysulfone (Udel <sup>®</sup> U.C.) <sup>12</sup>	Degrease in alcohol.	(A) Grit-blast with 27–50 μm aluminum oxide. (B) Etch in sodium dichromate-sulfuric acid soln. (C) Corona or plasma treatment	(A) • Clean in ultrasonic cleaner in Neutra-Clean (Shipley Co., Inc.) • Rinse in tap and then DI water. • Rinse in IPA for 30 seconds. • Flush with dry N <sub>2</sub> . • Dry in air at 150°F (66°C). (B) See Polyaryl sulfone treatment.

## Surface Treatment — Thermosets.

<i>Adherend Material</i>	<i>Cleaning</i>	<i>Abrasion or Chemical Treatment</i>	<i>Method</i>
Epoxy, epoxide resins	Degrease with acetone or MEK.	Abrade using medium-grit emery paper.	• Repeat degreasing step.
Furane resins	Degrease with acetone or MEK.	Abrade using medium-grit emery paper.	• Repeat degreasing step.
Melamine formaldehyde plastics (Formica)	Degrease with acetone or MEK.	Abrade using medium-grit emery paper.	• Repeat degreasing step.
Phenolics, polyester poly- urethane resins	Degrease with acetone or MEK.	Abrade using medium-grit emery paper.	• Repeat degreasing step.
Polyimide (Vespel® DuPont) <sup>12</sup>	(A) Degrease in trichloroethane (B) Degrease in acetone.	(A) Abrade with dry or wet abrasive blast. (B) Etch solution: Sodium hydroxide Water	(A) • Repeat degreasing. • Dry. (B) 5 pbw 95 pbw • Etch for 1 min at 140–194°F (60–90°C). • Rinse in cold water. • Dry in hot air.

## Surface Treatment—Carbon and Carbon Fiber and Glass Fiber Composites.

<i>Adherend Material</i>	<i>Cleaning</i>	<i>Abrasion or Chemical Treatment</i>	<i>Method</i>
Carbon	Degrease with acetone or MEK.	Abrade using fine-grit emery paper.	<ul style="list-style-type: none"> <li>• Repeat degreasing step.</li> <li>• Allow solvent to evaporate.</li> </ul>
Glass reinforced laminates	Degrease with acetone or MEK.	Abrade using medium-grit emery paper.	<ul style="list-style-type: none"> <li>• Repeat degreasing step.</li> </ul>
Graphite	Degrease with acetone or MEK.	Abrade using fine-grit emery paper.	<ul style="list-style-type: none"> <li>• Repeat degreasing step.</li> <li>• Allow solvent to evaporate.</li> </ul>
Carbon fiber-epoxy composites <sup>12</sup>	<p>(A) Solvent wipe (MEK, toluene, trichloroethylene, etc.)</p> <p>(B) Use peel ply during initial curing.</p> <p>(C) See Ref. 15 for the effect of abrasion procedures. See also Refs. 16 and 17.</p>	<p>(A) Lightly abrade with medium-grit emery paper. Avoid exposing the reinforcing fibers.</p> <p>(A)</p>	<ul style="list-style-type: none"> <li>• Wipe with solvent.</li> <li>• Check surface by water break test. Retreat, if necessary.</li> </ul>
Carbon fiber-polyether ether-ketone (PEEK <sup>®</sup> )	Solvent wipe with MEK.	<p>Abrade lightly with Scotch-brite-Bon Ami. Good strengths require (A) or (B) treatment:</p> <p>(A) Chromic acid etch: Exact composition of etch solution not defined in Ref. 18.</p> <p>(B) Plasma treatment gave good bond strengths also.</p> <p>(A)</p>	<ul style="list-style-type: none"> <li>• Rinse in tap water and DI water.</li> <li>• Air dry.</li> <li>• Immerse for 15 min at room temp.</li> <li>• Rinse in tap and then DI water.</li> <li>• Dry at 200°F (93°C) for 30 min.</li> </ul>

**Surface Treatment—Rubbers.**

<i>Adherend Material</i>	<i>Cleaning</i>	<i>Abrasion or Chemical Treatment</i>	<i>Method</i>
Rubber—natural and synthetic chloroprene, neoprene	Degrease with methyl alcohol.	For maximum strength use:  Chemical etch: Bath 1, concentrated sulfuric acid.  Neutralizing solution: Bath 2, 0.2% solution of caustic.	<ul style="list-style-type: none"> <li>• Immerse for 5–10 min in conc. sulfuric acid at 77°F (25°C) (Bath 1).</li> <li>• Wash thoroughly in cold DI water.</li> <li>• Neutralize by immersing for 5–10 min. at room temp. (Bath 2).</li> <li>• Rinse with cold, running DI water.</li> <li>• Dry.</li> </ul>

**Surface Treatment—Ceramics, Glass, etc.**

<i>Adherend Material</i>	<i>Cleaning</i>	<i>Abrasion or Chemical Treatment</i>	<i>Method</i>
Ceramics, porcelain, glazed china	Degrease with MEK.	Abrade using emery paper or sandblasting.	<ul style="list-style-type: none"> <li>• Repeat degreasing step.</li> <li>• Evaporate the solvent.</li> </ul>
Glass, quartz—nonoptical	Degrease with MEK.	<p>(A) Abrade using carborundum powder and water or fine-grit paper.</p> <p>(B) For maximum strength, continue abrading and use chemical etch:</p> <p>Chromium trioxide DI water</p> <p>1 pbw 4 pbw</p>	<p>(A)</p> <ul style="list-style-type: none"> <li>• Repeat degreasing step.</li> <li>• Dry for 30 min at 210°F (100°C).</li> </ul> <p>(B)</p> <ul style="list-style-type: none"> <li>• Immerse for 10–15 min at 77°F (25°C). Wash well in running water</li> <li>• Dry for 30 min at 210°F (100°C).</li> <li>• Apply adhesive while still hot.</li> </ul>
Glass—optical	Degrease in an ultrasonically agitated detergent bath.		<ul style="list-style-type: none"> <li>• Rinse thoroughly.</li> <li>• Dry &lt; 100°F (38°C).</li> </ul>
Jewels	Degrease with MEK.		<ul style="list-style-type: none"> <li>• Dry at room temp.</li> </ul>

Surface Treatment—Construction Materials.

<i>Adherend Material</i>	<i>Cleaning</i>	<i>Abrasion or Chemical Treatment</i>	<i>Method</i>
Bricks: Fired, nonglazed building materials	Degrease in acetone or MEK.	Abrade using a wire brush.	<ul style="list-style-type: none"><li>• Remove all contaminants.</li></ul>
Concrete	Decontaminate with a detergent so- lution.	Clean by one of these procedures: (A) Sandblast about 1/16" from bonding surface. (B) Remove 1/8 by mechanical scarification. (C) Chemical etch, hydrochloric acid solution (15% by wt.).	<ul style="list-style-type: none"><li>• Wash thoroughly with water.</li><li>• Remove all dust.</li></ul> <p>(C)</p> <ul style="list-style-type: none"><li>• Spread solution with a stiff bristled broom.</li><li>• Remove sludge with water from high pres- sure hose.</li><li>• Check with litmus paper for residual acid.</li><li>• If present, rinse with 1 % ammonia.</li><li>• Flush with water.</li><li>• Allow to dry.</li></ul>
Stonework	Dry thoroughly.	Abrade using a wire brush.	<ul style="list-style-type: none"><li>• Remove all contaminants.</li></ul>
Wood	Dry thoroughly.	Decontaminate with a sander, plane, smooth with sandpaper.	<ul style="list-style-type: none"><li>• Remove all contaminants.</li></ul>

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# Adhesive Selection and Screening Testing

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## INTRODUCTION

Selecting a proper adhesive for a given bonding application can, at times, appear to be an overwhelming task, but it need not be. The purpose of this chapter is to help in the selection process by:

1. Listing and briefly describing key material and system factors which should be considered during adhesive selection.
2. Outlining steps in the preliminary adhesive selection process.
3. Describing basic test methods which are useful in screening the candidate adhesives, once they have been chosen.
3. If the adhesive's hardening involves significant film shrinkage, the system (adhesive and/or adherend) should allow for dissipation of the shrinkage stresses rather than locking them in and prestressing the joint.
4. The rheology of the hardened adhesive film, especially its elastic modulus and toughness (versus brittleness), should be compatible with those of the adherend and the nature of joint stresses to be applied, etc.
5. The adhesive should *wet* the adherend, i.e., be able to establish extensive and intimate (molecular scale) interfacial contact with the substrate.

## GENERAL CONSIDERATIONS IN ADHESIVE SELECTION

An adhesive should be compatible with the materials it will join (i.e., its substrates/adherends):

1. When a liquid adhesive is involved, the adherend(s) should allow the carrier (solvent or water) to escape as needed for proper film forming and hardening.
2. The adhesive should not significantly attack or corrode the adherends.

The adhesive should work efficiently with the equipment which will be available for bonding (clamps, presses, heaters, etc.) and not have pressure, temperature or curing requirements which are beyond the limits of that equipment.

The adhesive must have adequate basic strength for its intended job. This often means strength as determined under short-term loading (most standard strength tests are in this category), but long-term loading (creep tests), shock loading (impact tests), and cyclical load-

ing (fatigue tests), or combinations of these, may also be needed.

In addition to adequate basic strength, the adhesive must be sufficiently durable to provide adequate load bearing ability when the joint is exposed to hostile elements of the environment in which it will serve.

The physical properties (e.g., color, density, solids or filler content, electrical properties, etc.) and working properties (storage life, pot life, viscosity, etc.) often need to be considered and subjected to screening testing too.

Last in this list, but often foremost in the user's mind, is bonding cost. Although many factors influence the ultimate bonding cost, the price per unit of adhesive is significant and must be considered early in the selection process.

## BASIC STEPS IN THE ADHESIVE SELECTION PROCESS

### Step 1

*Define* pertinent material, joint stress, joint exposure, processing and service variables relating to adherends, to joint design and loading, and to available bonding equipment. Of particular interest are the following:

- A. *Composition and properties of the substrate or substrates to be bonded.* Included are such factors as chemical composition (type of metal, plastic, ceramic or wood, etc.; special surface treatments, etc.); porosity and absorbency; hygroscopic and/or thermal expansivity; and strength properties.
- B. *Joint design and associated glueline stresses* (shear, tension, cleavage, creep, shock, vibration, etc.).
- C. *Hostile elements of the joint's service environment* (temperature and moisture extremes, chemicals, light, etc.).
- D. *Heating, pumping, and dispensing capabilities* of adhesive handling and application equipment available or affordable.
- E. *Clamping, pressing, and heating capabilities* of the available or affordable bonding equipment.

### Step 2

Based on the above determinations and in consultation with potential adhesive suppliers, select, first, the candidate adhesive group(s) and then the specific adhesives which may meet your requirements, i.e., be compatible with your adherends, joint design and stresses, exposure requirements, bonding equipment, physical and working property requirements, and cost limitations. This search can be aided by published articles, books, and catalogings of adhesives but, most importantly, by adhesive supplier recommendations, literature, and data sheets. In addition, occasions may arise when the services of an adhesives consultant may be in order, especially if they are also capable of performing needed screening testing.

A list of general adhesive information sources is given in Appendix 1 of this chapter. Several of the references cited give specific adhesive supplier names, addresses and phone numbers and product use listings. These listings can be a good starting point in making initial supplier contacts and in beginning to generate a list of candidate adhesives.

### Step 3

Carefully compare your material and system characteristics with the relevant properties of selected or recommended adhesives.

Your suppliers will have already thought through the previously listed considerations relative to their products and be glad to discuss them with you. The adhesive composition and properties factors of primary interest include the following:

1. *Adhesive form and, if a liquid, the nature of any solvents or carriers involved.* Most adhesives are supplied and used as liquids. However, they may also be supplied as meltable solids in many forms (e.g., chunk, pellet, rope, cartridge, etc.) and as flowable or fusible powders or films. Some liquid adhesives may be essentially 100% reactive and contain little or no solvent or carrier. However, most liquid adhesives contain significant portions of carrier (water or other solvents) which normally must be largely gotten rid of during hardening.
2. *The adhesive's hardening mechanism and*

*chemistry.* During bond formation, an adhesive must initially be fluid or semi-fluid in order to wet and make good interfacial contact with the substrate. But then it must harden to develop strength and durability. The hardening process is a key property of the adhesive, and the commonly encountered mechanisms are generally as follows:

- a. *Drying.* Many liquid adhesives harden simply by an increase in concentration of solids as the solvent or water evaporates into the surrounding atmosphere or is dispersed into the adherend(s).
- b. *Coalescence.* Emulsion adhesives initially harden by a process of coalescence as water in the continuous phase evaporates or disperses and the emulsion particles make contact. The coalesced film will then harden further as remaining moisture is dissipated. Chemical reactions may also be involved.
- c. *Chemical Reaction.* Many adhesives harden either totally or in part by chemical reaction (usually polymerization) occurring primarily during bonding.
- d. *Congeeing/freezing.* Some adhesives are applied warm or hot and harden, wholly or in part, by congealing as they cool off on the adherends. Hot melt adhesives in particular are applied quite hot and harden very quickly as they cool off. Dry film adhesives have initially meltable or flowable characteristics and may harden initially by cooling off, but with chemical reaction involved too.

3. *Strength and durability of the adhesive under various stress modes* (tension, shear, creep, impact, cyclic, etc.) *and stress levels* (low, medium, high, etc.) in the intended joint design and when under the influence of the intended service environment. Although we may speak of the strength and durability of the adhesive, it must be emphasized that it is the serviceability and reliability of the *joint* or *bonded assembly* that we are ultimately interested in. It is not at all difficult to take an adhesive with excellent potential and use it in an improper application or with poor bonding technique and make a very poor joint.

#### Step 4

Select and perform screening tests on candidate adhesives.

When one or more adhesives have been chosen as candidates for a given bonding application, samples should be obtained and joints, representative of intended production, made and tested. Testing will usually be done to measure strength and/or durability. However, testing for physical and working properties may also be desirable. Some test procedures call for equipment not routinely available in all user laboratories. In those cases, the services of an independent testing laboratory should be considered.

Selecting appropriate screening tests is not always easy, but familiarity with the tests available and their use will simplify matters. Appendix 2 of this chapter is a complete listing of standards currently under the jurisdiction of ASTM Committee D-14 on Adhesives (plus a few adhesive standards from other ASTM committees) and should be helpful in looking for appropriate screening tests.

Appendix 2 first lists ASTM's adhesive performance specifications, most of which are in the area of wood bonding. They are subdivided by substrate or application. Whenever a specification is available for the adhesive or bonding application being considered, it should certainly be used in the screening testing if at all possible.

The bulk of Appendix 2 is comprised of methods of test (as distinct from specifications). They are classified first by substrate (metal, wood, plastics, etc.) and then, within substrate, by primary test objective (strength or durability). The strength test listings are further subdivided by stress mode (tension, shear, peel, etc.) and with separate listings for creep, impact, and fatigue tests.

A number of standard test methods and practices have been developed to measure (a) the composition of glue mixes (especially polymer and/or filler/extender content) and (b) the rheological and working properties of adhesives (viscosity, density, tack, etc.). They are listed in Appendix 2 by these property groupings.

Most of the remainder of this chapter is devoted to a review and discussion of the key

D-14 strength and durability tests as they apply to various adhesives and applications. But first, some general precautions on the preparation of trial joints and their testing are in order.

### GENERAL PRECAUTIONS IN PREPARING AND TESTING ADHESIVE BONDED JOINTS

Successful adhesive testing depends not only on starting with the right adhesive but also on proper (a) preparation of the adherends, (b) mixing and application of the adhesive, (c) clamping of the joint and curing of the adhesive, (d) test specimen preparation, and (e) test execution. Specific points to be careful about are given below.

#### Adherend Preparation

For best results, the adherends should (1) be manufactured and/or machined with dimensional accuracy such that, when clamped or pressed, the joint can be closed uniformly, bringing the two surfaces into intimate contact, and (2) be cleaned, machined, or treated as necessary to present a sound, clean bonding surface to the adhesive.

For metals and plastics in particular, pre-bonding chemical treatment of adherend surfaces is often necessary. The success of high performance metal bonding is so heavily dependent on proper surface preparation that several ASTM standards have been developed which describe procedures for surface treatment and for analysis of the chemicals involved:

1. Standards relating to the surface treatment of metal adherends:  
D-2651. "Practice for Preparation of Metal Surfaces for Adhesive Bonding." Includes procedures for washing, steaming, solvent cleaning (degreasing), mechanical abrasion and chemical treatment or etching.  
D-2674. "Methods of Analysis of Sulfochromate Etch Solution Used in Surface Preparation of Aluminum."  
D-3933. "Practice for Preparation of Aluminum Surfaces for Structural Adhe-

sives Bonding (Phosphoric Acid Anodizing)." Outlines the relatively new phosphoric acid anodizing procedure.

2. Standards evaluating the effectiveness of surface treatment of aluminum adherends by means of resultant bond durability:  
D-3762. "Test Method for Adhesive-Bonded Surface Durability of Aluminum (Wedge Test)." Commonly used to monitor the effectiveness of metal surface treatment in preparation for high durability, high performance adhesive bonds. A wedge is driven into a prepared opening in the glue line and the extent of resultant crack propagation measured.
3. Standard relating to the surface treatment of plastics in preparation for adhesive bonding:  
D-2093. "Practice for Preparation of Surfaces of Plastics Prior to Adhesive Bonding." Suggests sanding, solvent wiping and chemical pretreatments to remove glossy finishes, dirt, grease, mold release compounds, etc. in preparing plastics for effective adhesive bonding.

#### Adhesive Handling, Preparation, and Application

Follow the suppliers' literature, instructions sheets and precautions, paying close attention to:

1. *Storage temperature extremes or high humidity.* Very low temperatures can especially damage emulsion adhesives, and high temperatures will generally cause premature polymerization of reactive adhesives. High humidity most often creates problems with adhesives (or their fillers and extenders) purchased in dry form and stored in containers permeable to moisture vapor.
2. *Proportioning and mixing procedures.* When an adhesive is to be mixed, the components should be accurately measured, and mixing should be of the recommended type and intensity. The objective is to achieve a uniform, lump-free mix without overheating, entraining air (unless a foam-type mix is intended)

or degradation from excessive mixing shear (a special concern with emulsion systems).

3. *Proper application of adhesive to adherend.* The keys to proper application are very simply an adequate amount of adhesive, accurately and uniformly applied.

### Joint Assembly and Handling

The joints to be bonded should be formed and clamped or pressed within the allowable assembly times (minimum and maximum, but especially maximum) and conditions (especially temperature). With some chemically curing adhesives, prolonged assembly times, especially at high ambient or adherend temperatures may lead to precure (i.e., hardening before the joint is properly closed), resulting in very poor bonds. Also, with hot melt adhesives, which harden quickly as they cool below their melt temperature, allowable assembly ("open") times are very short and must be very carefully observed.

### Clamping/Pressing and Curing

Bonding pressure should be adequate but not excessive. Bondline temperatures and times under pressure should be adequate to achieve at least nominal cure.

### Careful Specimen Preparation and Test Execution

Care must be taken in specimen geometry and machining and in testing and alignment if stressing is to be as intended by the test.

### SCREENING ADHESIVES COVERED BY STANDARD SPECIFICATIONS

Standard specifications (as distinct from standards which are methods of test only) include (or reference) appropriate test methods and also set forth minimum acceptable performance. Various industry groups have their own application-oriented specifications (e.g., aerospace, automotive, plywood, laminated wooden beams, etc.; see documents cited in Appendix 1). However, discussion here is limited to those

specifications which have been developed and/or adopted by ASTM.

### Construction Adhesives

In recent years the use of adhesives in construction assembly applications, especially in the bonding of wood and gypsum panels to joists and studs in floors, walls and ceilings, has increased considerably. Several specifications and related test methods have been developed:

C-0557. "Specification for Adhesives for Fastening Gypsum Wallboard to Wood Framing." Describes test methods and establishes minimum performance requirements for various working and performance (strength and durability) properties.

D-1779. "Specification for Adhesive for Acoustical Materials." Tests primarily for minimum long term gluebond tensile strength after exposure to a variety of simulated average and extreme environments.

D-2851. "Specification for Liquid Optical Adhesive." For adhesives used in bonding glass and other transparent adherends in optical assemblies.

D-3498. "Specification for Adhesives for Field-Gluing Plywood to Lumber Framing for Floor Systems." Tests construction assembly adhesives for minimum shear strength and permanence (including oxygen bomb aging).

D-3930. "Specification for Adhesives for Wood-Based Materials for Construction of Manufactured Homes." Tests for minimum levels of strength and permanence for adhesives used in structural and semistructural (mainly panel to frame) gluing in manufactured housing (modular and mobile homes). Also referenced are standards D-3632, "Practice for Accelerated Aging of Adhesive Joints by the Oxygen-Pressure Method," and D-3931, "Test Method for Determining Strength of Gap-Filling Adhesive Bonds in Shear by Compression Loading."

## Wood Bonding Adhesives

Standards covering adhesives for various end-glued (finger-jointed), edge- and face-bonded joints.

D-2559. "Specification for Adhesives for Structural Laminated Wood Products for Use Under Exterior (Wet Use) Exposure Conditions." Sample beams, made under various assembly time extremes, are tested for (a) basic dry glue-line shear strength and wood failure and (b) resistance of glue-line to delamination after accelerated aging. It also requires testing the adhesive's dry creep resistance. Used in qualifying new adhesives for use in exterior laminated beams.

D-3024. "Specification for Protein-Base Adhesives for Structural Laminated Wood Products for Use Under Interior (Dry Use) Exposure Conditions." Employs the D-0905 block shear, D-0906 plywood shear, and D-4300 mold resistance tests to evaluate mostly *casein-base* adhesives for use in interior grade laminated beams.

D-3110. "Specification for Adhesives Used in Nonstructural Glued Lumber Products." Employs the D-0905 block shear test and a finger joint test, along with several exposures, to evaluate interior and semi-exterior adhesives, in end, edge and face bonded joints, especially for the molding and millwork field. Most of the applicable adhesives are based on polyvinyl acetate.

D-4317. "Specification for Polyvinyl Acetate-Based Emulsion Adhesives." Somewhat similar in scope to D-3110, this standard employs the D-0905 block shear and D-0906 plywood shear tests in evaluating polyvinyl acetate based adhesives for common wood gluing applications.

D-4690. "Specification for Urea-Formaldehyde Resin Adhesives." Recent standard providing specific test procedures and minimum performance require-

ments for urea-formaldehyde resin adhesives used in wood gluing.

## Paper Bonding Adhesives

Most standards in this area have been promulgated by TAPPI. The few which have been promulgated by ASTM are as follows:

D-1580. "Specification for Liquid Adhesives for Automatic Machine Labeling of Glass Bottles." For non-pressure-sensitive adhesives.

D-1874. "Specification for Water- or Solvent-Soluble Liquid Adhesives for Automatic Machine Sealing of Top Flaps of Fiberboard Shipping Cases." For non-pressure-sensitive adhesives.

## TESTING FOR THE STRENGTH OF ADHESIVE BONDED JOINTS

In contrast to the preceding, there are many adhesives and applications for which we do not have specification documents. However, there are numerous standards which can be applied in a general purpose testing manner, and they are discussed in the following section.

## Tensile Properties

Although shear testing may be more commonly used, stressing perpendicular to the glue-line may be called for at times. The following two general-purpose tensile test standards can be used with various substrates, including metal, wood, and plastics:

D-0897. "Test Method for Tensile Properties of Adhesive Bonds." Fig. 1 shows this basic ASTM standard's two specimen configurations which can be used in the comparative testing of wood- and metal-bonding adhesives, respectively. However, research evidence suggests that significant stress concentrations commonly occur in the tensile testing of butt joints of this type. Extrapolation of stress values derived from this test to different bond areas or configurations can be very misleading. Recent work has shown that much more

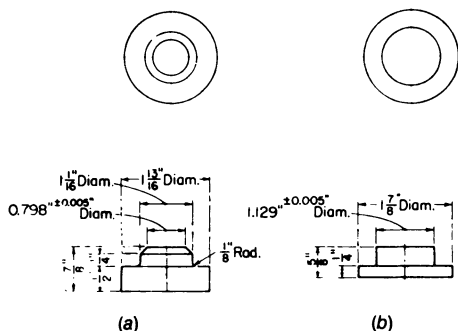


Fig. 1. Tension specimens: (a) wood and (b) metal (D-0897).\*

carefully designed joints and controlled stressing are necessary if anything like “pure” tensile stress data are to be achieved.

\*All figures in Chapter 5 are reprinted, with permission, from the Annual Book of ASTM Standards, copyright, the American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103-1187.

D-2095. “Test Method for Tensile Strength of Adhesives by Means of Bar and Rod Specimens” (and the companion standard D-2094: “Practice for Preparation of Bar and Rod Specimens for Adhesion Tests”). This specimen (shown, with grips, in Fig. 2) should be easier to prepare than the preceding one. It seems to be in more common use today, and is especially useful with metal and plastic substrates. As with D-0897, significant stress concentrations can develop, and extrapolation of test data to other joint configurations or bond areas should be approached with care.

### Shear Properties

Many adhesive bonded assemblies are designed to take advantage of the generally good resistance adhesive joints have to shear stresses.

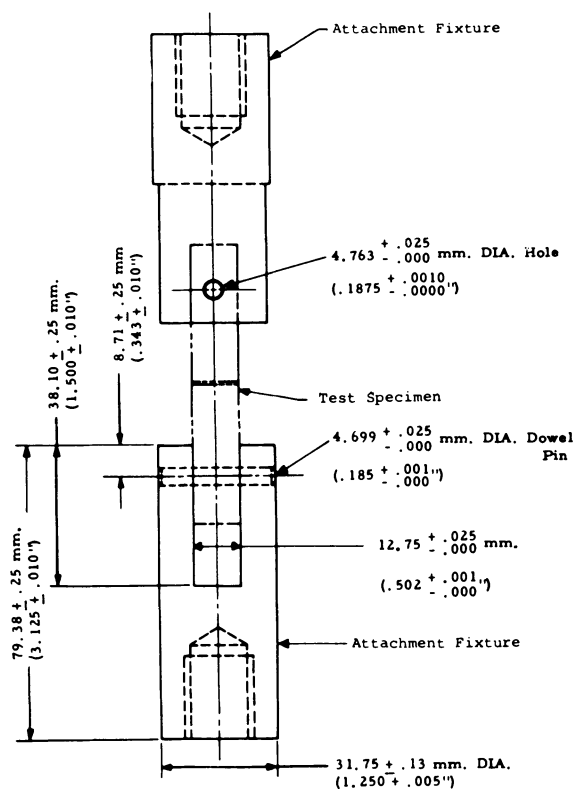


Fig. 2. Bar and rod specimen and grips (D-2095).

**Shear Load at Rupture.** *Tests which use tension loading.*

1. Single lap tensile shear tests for metal adherends:

D-1002. "Test Method for Strength Properties of Adhesives in Shear by Tension Loading (Metal-to-Metal)." This is another of D-14's earlier standards and may still be the most widely used in screening metal bonding adhesives. The matter of stress concentrations (especially edge effects) and associated limitations on interpretation and extrapolation of data from this test have been widely studied and clearly recognized. However, the specimen (Fig. 3) is relatively easy to prepare, and the test has still proven useful. Standards D-2295 and D-2557 are the procedures for running D-1002 at elevated and reduced temperatures, respectively.

D-3165. "Test Method for Strength Properties of Adhesives in Shear by Tension Loading of Laminated Assemblies." Fig. 4 shows this single lap shear specimen which is prepared by machining notches into strips from laminated metal sheets.

2. Single lap tensile shear for wood adherends:

D-2339. "Test Method for Strength Properties of Adhesives in Two-Ply Wood Construction in Shear by Tension Loading" (Fig. 5). Useful with laminations of veneers or other relatively thin sheets of wood.

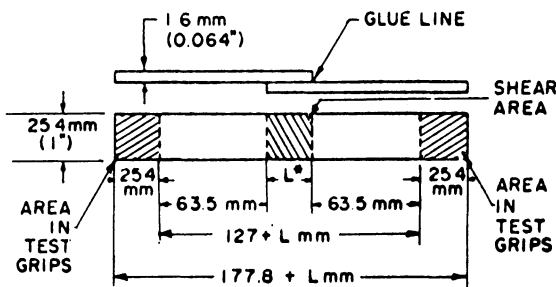


Fig. 3. Basic metal lap shear specimen (D-1002).

3. Double lap tensile shear for metal adherends:

D-3528. "Test Method for Strength Properties of Double Lap Shear Adhesive Joints by Tension Loading." The two specimens in this test both use a more balanced, double lap design (see Fig. 6 as example), alleviating some of the distortion and cleavage stressing which easily occurs with standard single lap shear specimens. However, the problems associated with testing two or more gluelines at one time now come into play and might complicate comparative testing.

4. Plywood shear test:

D-0906. "Test Method for Strength Properties of Adhesives in Plywood Type Construction in Shear by Tension Loading." Fig. 7 shows the specimen for this widely used test. In common usage, the main test criterion is a visual estimate of the area percentage of rupture failure which occurs as "wood failure" (versus "glue failure") and not the measured joint strength.

5. Testing structural finger joints:

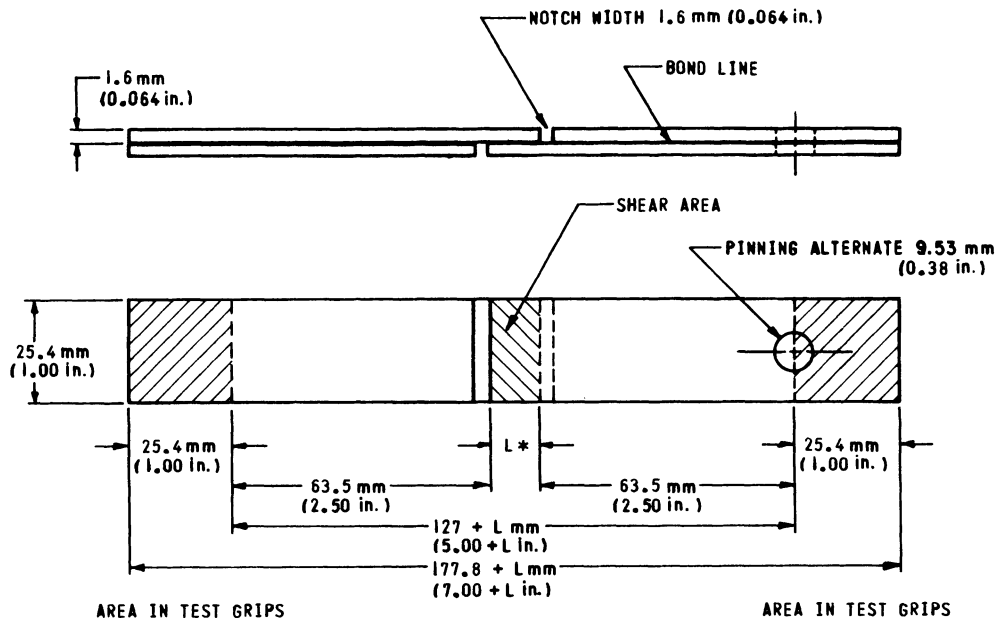
D-4688. "Test Methods for Evaluating Structural Adhesives for Fingerjointing Lumber." A recent standard detailing the testing of finger joints when used as end joints in structural glued, laminated timbers (see also D-2559 in wood adhesive specifications).

*Tests where adherends are loaded in compression:*

1. Wood block compression shear:

D-0905. "Test Method for Strength Properties of Adhesive Bonds in shear by Compression Loading" (Fig. 8). A basic compression shear test which is widely used in screening wood glues. It is also used in specifications D-3110 (on nonstructural wood laminating adhesives), D-2559 and D-3024 (on exterior and interior structural wood laminating adhesives respectively) and D-4317 (on polyvinyl acetate based wood adhesives).





NOTE—\*L = length of test area. Length of test area can be varied. Recommended length of lap is  $0.50 \pm 0.01$  in. ( $12.7 \pm 0.3$  mm).

Fig. 4. Metal lap shear specimen cut from laminate (D-3165).

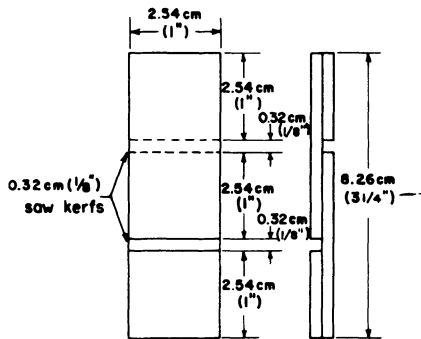


Fig. 5. Basic wood lap shear specimen (D-2339).

2. Block compression shear:  
D-4501. "Test Method for Shear Strength of Adhesive Bonds Between Rigid Substrates by the Block-Shear Method." Fig. 9 shows the two specimen configurations and the test head for this new, general-purpose, compression shear test which should be suitable for testing adhesives for plastics, metals, glass, wood, and other substrates.

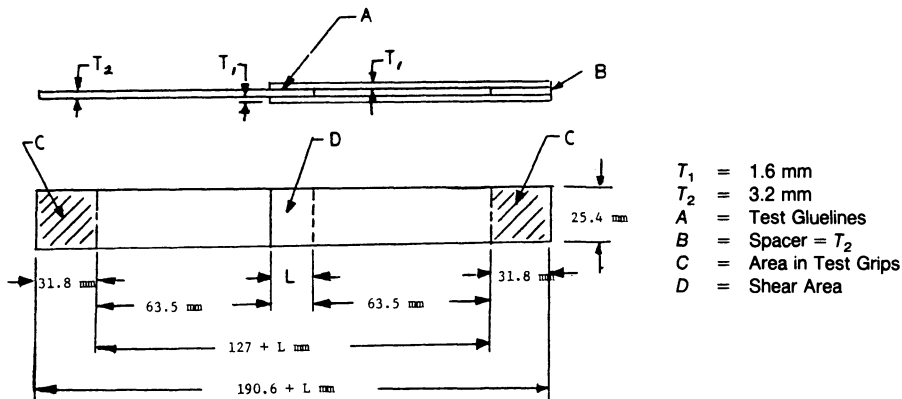


Fig. 6. Double lap shear specimen, Type A (D-3528).

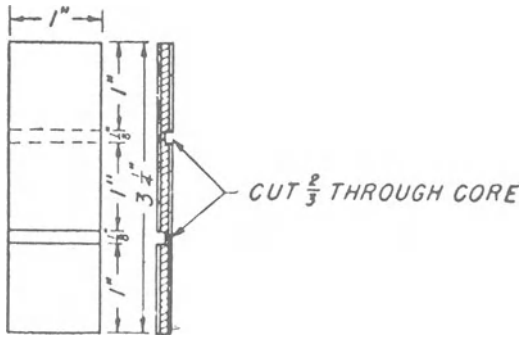


Fig. 7. Plywood shear specimen (D-0906).

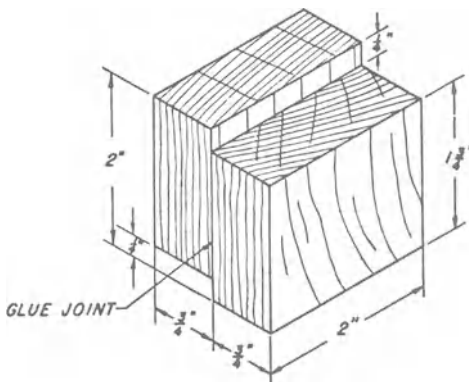
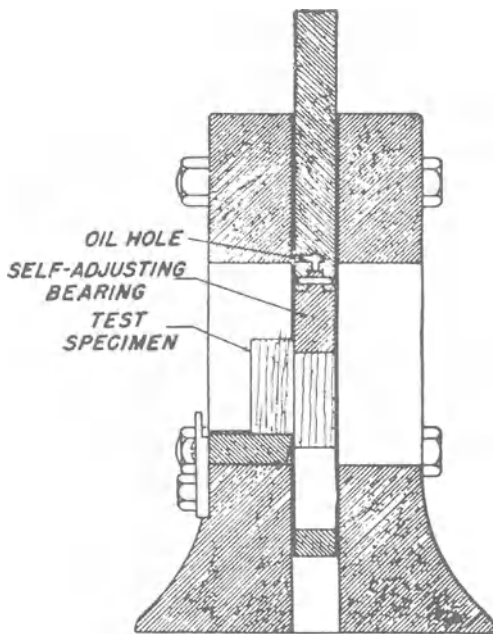


Fig. 8. Wood block shear test head and specimen (D-0905).

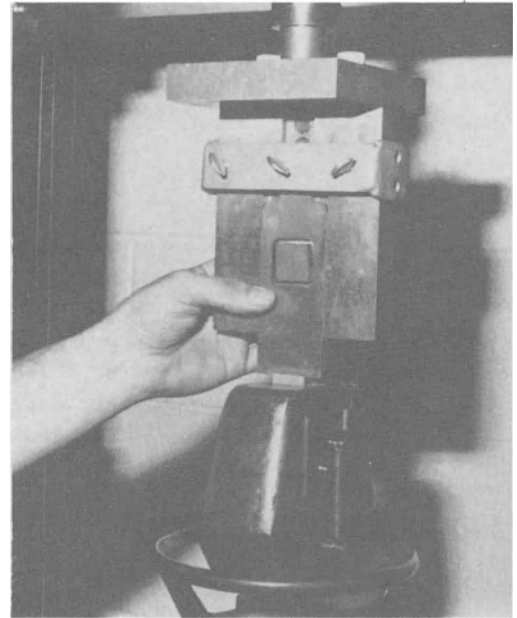
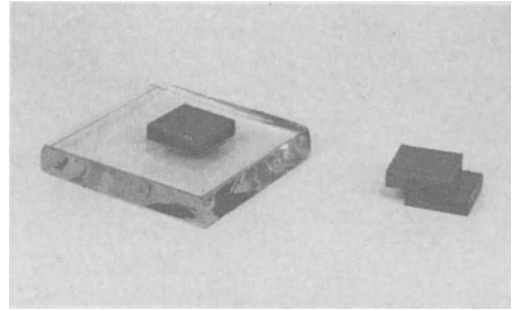


Fig. 9. New block shear specimens (top) and test head (bottom) (D-4501).

### 3. Pin and collar compression shear:

D-4562. "Test Method for Shear Strength of Adhesives Using Pin-and-Collar Specimen" (Fig. 10). Designed to yield data on the shear resistance of adhesive joints where a pin is bonded inside a collar. Particularly applicable to testing adhesives used as retaining compounds in nut locking and related applications.

### 4. Torque strength of UV cured glass/metal bonds:

D-3658. "Practice for Determining the Torque Strength of Ultraviolet (UV) Light-Cured Glass/Metal Adhesive Joints." Provides a method for measuring torsional shear strength of glass-to-metal bonds. The torque needed to

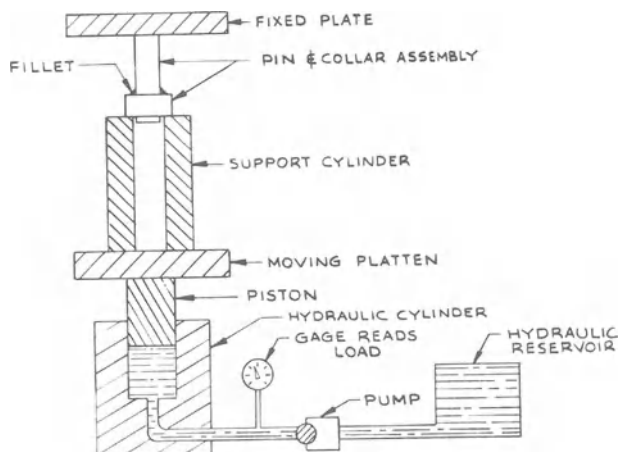


Fig. 10. Pin and collar shear specimen and test head (D-4562).

shear a metal hex nut off a glass surface is measured, usually as a function of cure time and UV exposure. Often used as a "fixturing time" test, i.e., to determine the minimum amount of time and UV exposure required to develop a "handling" bond with UV cured adhesives.

### Shear Modulus

D-3983. "Test Method for Measuring Strength and Shear Modulus of Non-rigid Adhesives by the Thick Adherend Tensile Lap Specimen" (Fig. 11). For measuring the properties of lower-modulus, more rubbery adhesive films. Glueline thickness is controlled by shims. Developed for wood but applicable to metals and other substrates also.

D-4027. "Test Method for Measuring Shear Properties of Structural Adhesives by the Modified-Rail Test." A rather involved test, especially with regard to the system of loading and mea-

surements and oriented more toward development of data on basic engineering parameters of the adhesive. Originally developed for use with wood but may be applicable to metals as well.

E-0229. "Test Method for Shear Strength and Shear Modulus of Structural Adhesives." This method employs torsional shear loading on a "napkin ring" specimen to determine the shear strength and shear modulus of structural adhesives in thin gluelines on high modulus adherends.

### Rate of Development of Shear Strength.

Standard D-1144, "Practice for Determining Strength Development of Adhesive Bonds," is based on the D-1002 lap shear specimen. Bonded metal specimens are tested in a cure time sequence.

### Strength in Bending

Occasionally, the property of interest may be resistance to bond failure when a laminate is loaded in bending. D-1184, "Test Method for

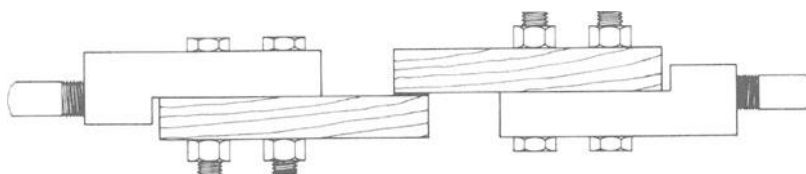


Fig. 11. Thick adherend lap shear specimen and grips (D-3983).

Flexural Strength of Adhesive Bonded Laminated Assemblies," is primarily applicable to wood and metal adherends.

### Peel Resistance

The testing of adhesive bonded joints in peel implies either (a) a flexible adherend being peeled from a rigid adherend or (b) two at least semi-flexible adherends being peeled from one another. Depending on the combination being dealt with, one or the other of the below-listed standards should be applicable to a variety of adherends.

D-0903. "Test Method for Peel or Stripping Strength of Adhesive Bonds." This is the standard 180° peel test (Fig. 12) applicable where one of the adherends is sufficiently flexible to endure the 180° fold back. Tests the resistance to peel separation of flexible foils, films, or tapes from relatively rigid base adherends (metal, wood, plastic, glass, etc. of adequate thickness).

D-1781. "Method for Climbing Drum Peel Test for Adhesives." Tests the resistance to removal in peel of less flexible adherends from relatively rigid substrates. Fig. 13 shows the test device, which is a bit complex but useful where peel resistance data are needed on bonds involving adherends too stiff for

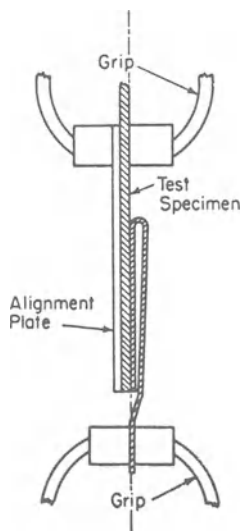


Fig. 12. 180° Peel specimen and grips (D-0903).

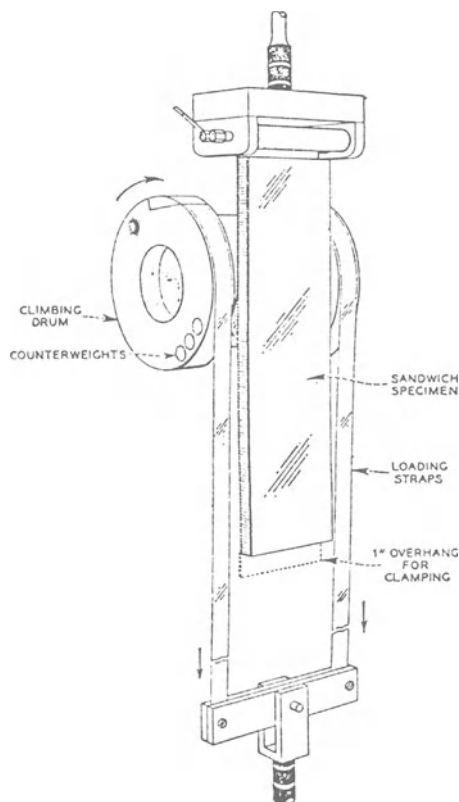


Fig. 13. Climbing drum peel specimen and loading device (D-1781).

the severe deformation of other peel tests. Especially intended for measuring resistance to peel separation of moderately flexible metal skins from sandwich panel cores (e.g., honeycomb).

D-1876. "Test Method for Peel Resistance of Adhesives (T-Peel Test). Tests resistance to peel separation in joints between two adherends which are flexible enough to deform into the T configuration (Fig. 14) without cracking or breaking (e.g., thin laminated aluminum sheets).

D-3167. "Test Method for Floating Roller Peel Resistance of Adhesives." Fig. 15 shows this specimen and device. Peel is achieved at a less-than-90° angle, but good axis-of-loading alignment is maintained over a significant bond length. Useful in peel testing semi-flexible surface adherends bonded to a rigid base adherends. Particularly applicable in testing peel resistance of flexible metals

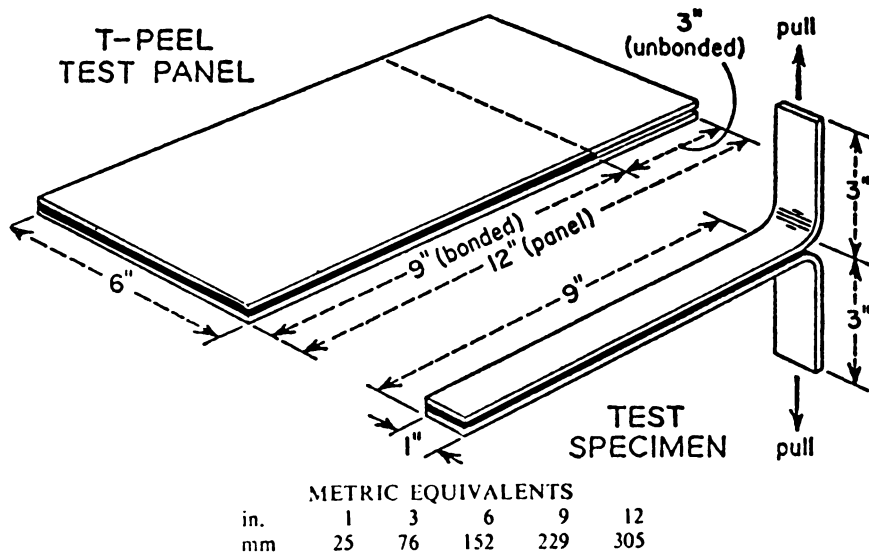


Fig. 14. T-peel panel and specimen (D-1876).

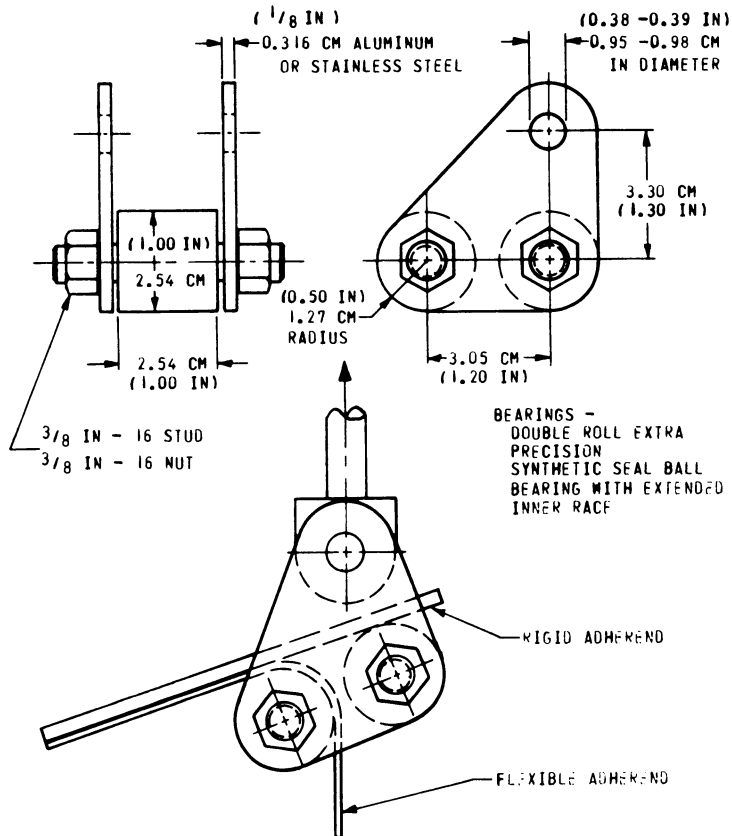


Fig. 15. Floating roller peel test head and specimen (D-3167).

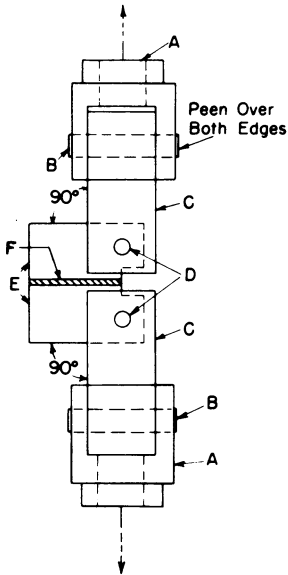
skins laminated to rigid metal substrates.

### Cleavage Strength

From the early days of adhesives testing it has been recognized that in-service loading on adhesive joints frequently subjects the bondline to cleavage stresses (more-or-less concentrated tensile stresses approximately perpendicular to the bondline). Thus another of D-14's earlier standards is D-1062, "Test Method for Cleavage Strength of Metal-to-Metal Adhesive Bonds." It employs a relatively simple specimen (Fig. 16) and loading procedure.

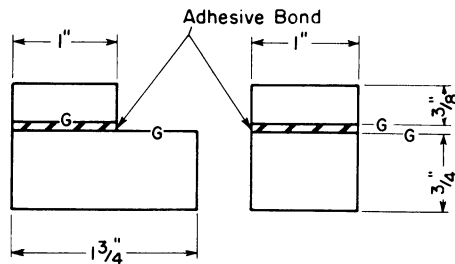
### Impact Strength

Joints often experience impact or shock loads, and their reactions will differ depending on the rheology of the adherend and the adhesive. Another early standard is D-0950, "Test Method for Impact Strength of Adhesive Bonds." It involves a relatively simple specimen (Fig. 17), but a special pendulum device is required for application of the impact shear load.

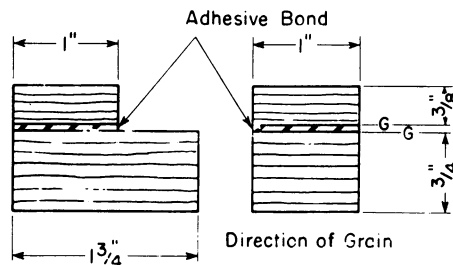


- A—Upper grip.
- B—Pin connecting upper and lower grips.
- C—Lower grip.
- D—Pin for attaching grip to specimen.
- E—Metal pieces.
- F—Glue line.

Fig. 16. Cleavage test specimen and grips (D-1062).

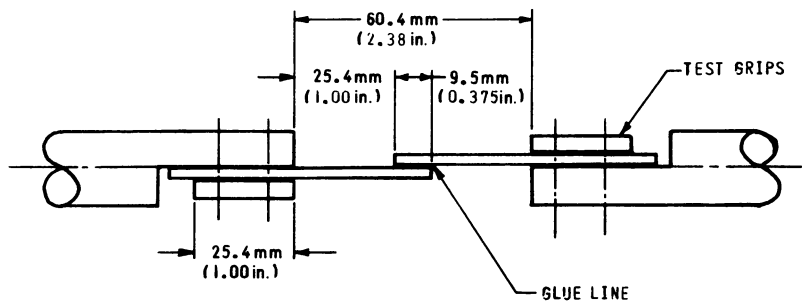


(a) Metal-to-Metal Specimen



(b) Wood-to-Wood Specimen

Fig. 17. Impact test specimens for (a) metal and (b) wood (D-0950).



NOTE—Minimum specimen length in the grip 25.4 mm (1 in.).

Fig. 18. Tension shear fatigue specimen and grips (D-3166).

### Fatigue Strength

Experience has shown that adhesive bonds can, over time, experience gradual deterioration and failure from cyclic loading and unloading, even when the individual load events are not in the range which would normally produce failure. Joints which experience significant vibration in service are likely to be the most susceptible to fatigue. In D-3166, “Test Method for Fatigue Properties of Adhesives in Shear by Tension Loading (Metal/Metal),” the specimen (Fig. 18) is a relatively simple one. However, loading calls for a tensile tester capable of applying a sinusoidal cyclic load at rates as high as 1800 cycles/minute or more.

### Creep

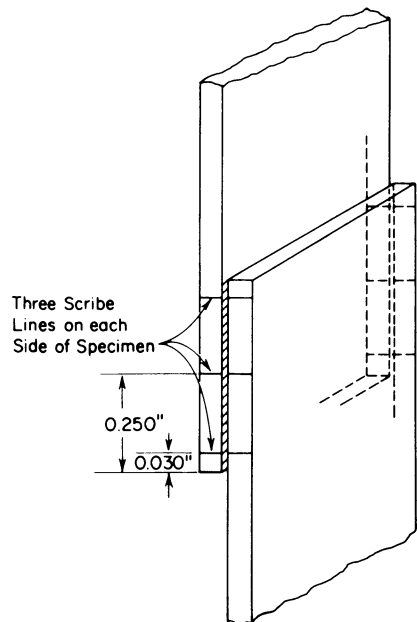
Long-term, viscoelastic deformation can be a problem with less rigid adhesives, even under moderate loads, and may need to be tested for.

D-1780. “Practice for Conducting Creep Tests of Metal-to-Metal Adhesives.” A general procedure for applying a constant tensile load to simple lap shear specimens (Fig. 19) and monitoring the scribed glue line edge, by microscope, for time-dependent deformation. Since temperature can have a marked affect on creep, requirements for isothermal testing are emphasized.

D-2293. “Test Method for Creep Properties of Adhesives in Shear by Compression Loading (Metal-to-Metal).” Fig. 20 shows the specimen and spring actuated loading device for

this test which also measures creep deformation along the bondline edge.

D-2294. “Test Method for Creep Properties of Adhesives in Shear by Tension Loading (Metal-to-Metal) (Fig. 21). The tensile creep counterpart to D-2293. D-4680. “Test Method for Creep and Time to Failure of Adhesives in Static Shear by Compression Loading (Wood-to-Wood)” (Fig. 22). A new compres-



Metric Equivalents

in.	0.030	0.762
mm	0.250	6.350

Fig. 19. Tension shear creep specimen for metal bonding adhesives (D-1780).

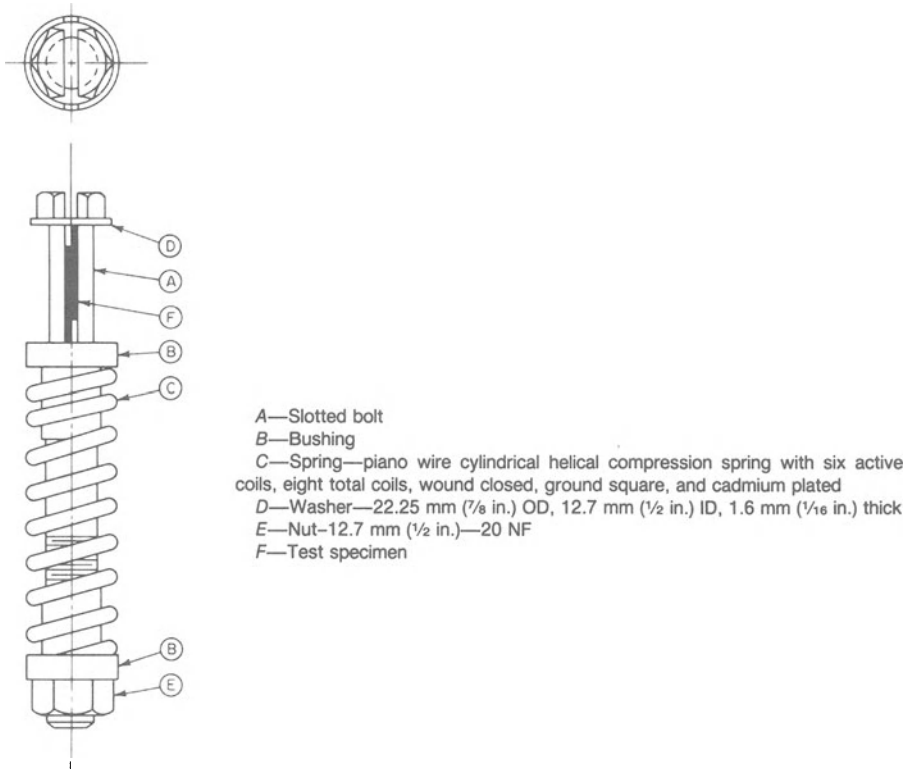


Fig. 20. Compression shear creep specimen and spring loading device for metal bonding adhesives (D-2293).

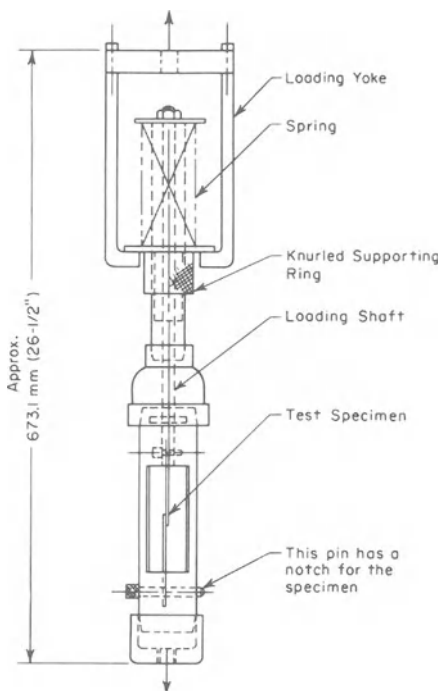


Fig. 21. Tension shear creep specimen and spring actuated loading device for metal bonding adhesives (D-2294).

sion shear creep and creep-fail test which uses a modified D-0905 block shear specimen to measure creep rate and time to failure, primarily on adhesives thought to have at least some creep tendency.

### Fracture Strength

As an outgrowth of interest in studying material failure via crack propagation, D-3433, "Practice for Fracture Strength in Cleavage of Adhesives in Bonded Joints," was developed. It describes specimen fabrication (Fig. 23) and testing, and calculation of the adhesive's fracture strength in cleavage.

### TESTING THE DURABILITY OF ADHESIVE BONDED JOINTS

#### Metal Bonding Adhesives

**Joint Strength Retained after Exposure to Hostile Environments.** In addition to initial strength, adhesive bonded joints should possess adequate durability and be able to maintain



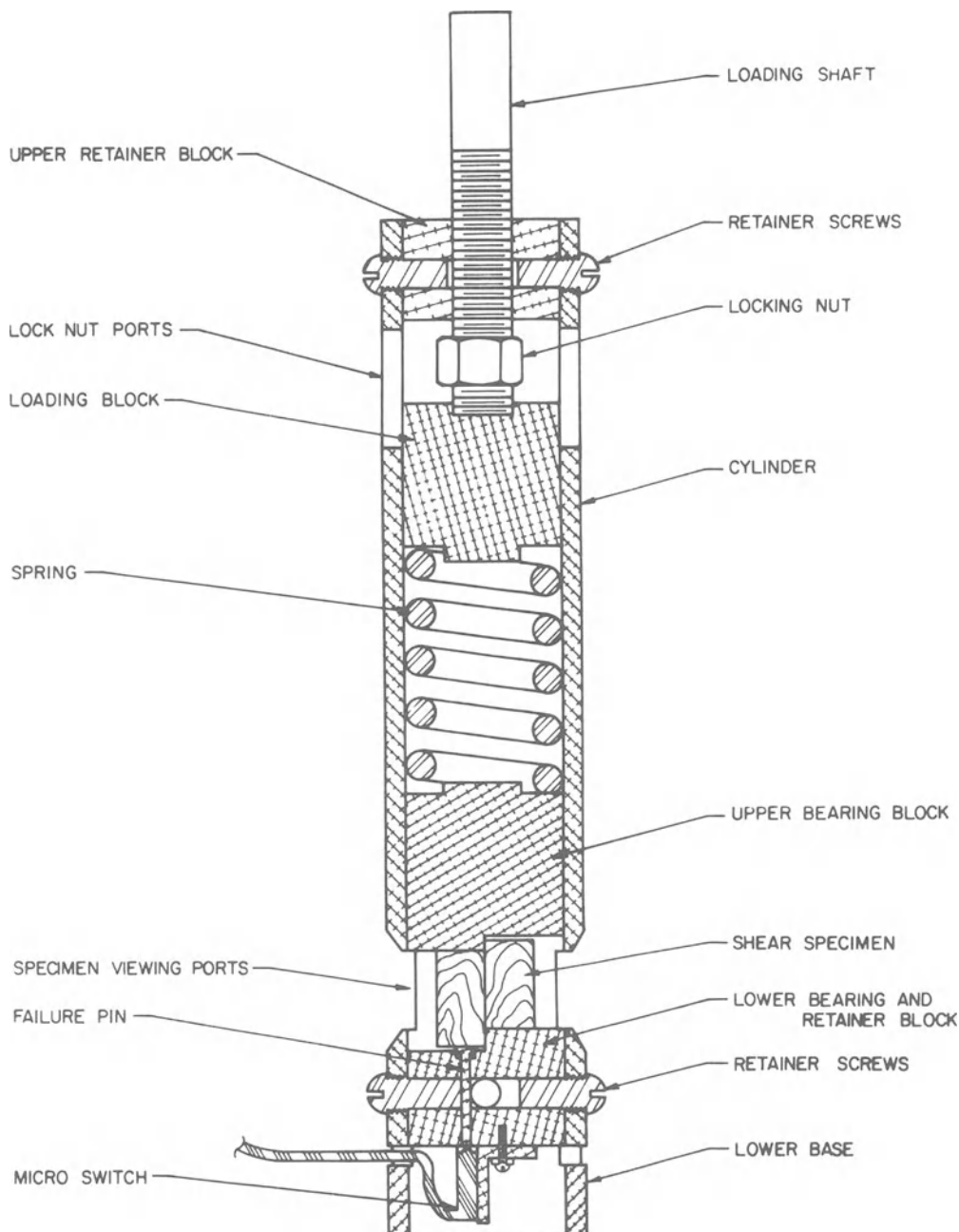


Fig. 22. New compression shear creep specimen and spring actuated loading device for wood bonding adhesives (D-4680).

needed load resistance over a reasonable service life when exposed to hostile elements of their service environment. Several of the durability-related D-14 standards are procedures for taking one or more of the previously described strength test specimens, adding expo-

sure to selected (generally somewhat harsh) environments, and then measuring resultant strength losses. The following standards describe exposure conditions, both artificial and natural, general and specific, which could be used with a variety of the previously described

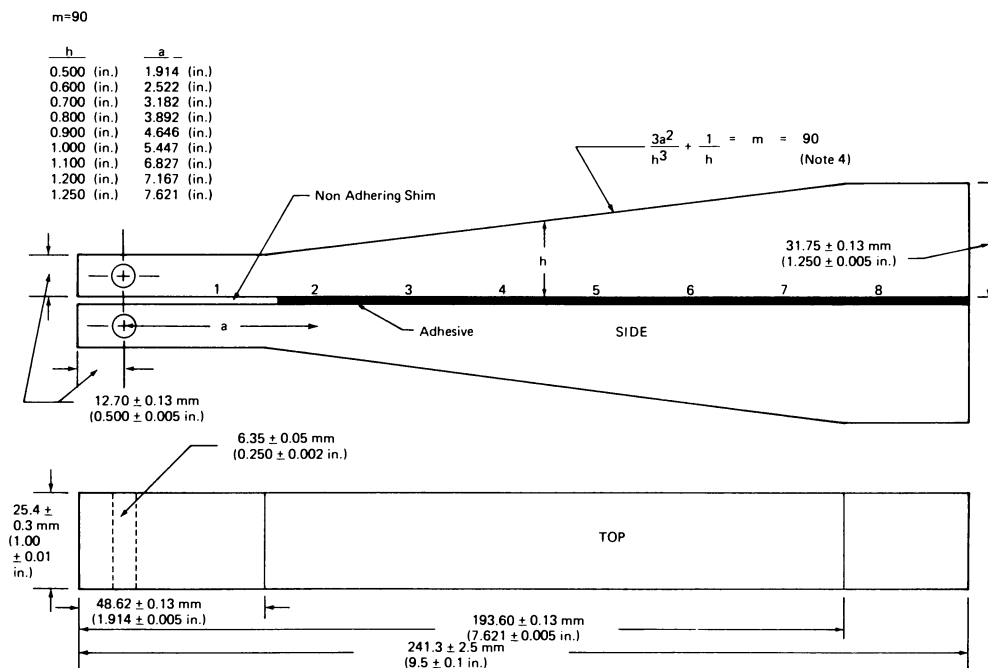


Fig. 23. Double cantilever fracture strength specimen (D-3433).

standard strength specimens to test for various aspects of durability.

D-0896. "Test Method for Resistance of Adhesive Bonds to Chemical Reagents." Suggests several chemicals which adhesives might be exposed to in testing and references the listings of others.

D-1151. "Test Method for Effect of Moisture and Temperature on Adhesive Bonds." Procedure for taking previously described basic tests and measuring strength loss as a function of time after exposure to defined temperature/humidity combinations. Some 22 sets of exposure conditions, ranging in temperature from  $-70^{\circ}\text{F}$  to  $+600^{\circ}\text{F}$  and variously including low humidity, high humidity, and water immersion, are suggested.

D-1183. "Test Methods for Resistance of Adhesives to Cyclic Laboratory Aging Conditions." Whereas D-1151 employs exposure to constant temperature and humidity environments, D-1183

exposes specimens to cycles of temperature/humidity. Four environments, two designated as "interior," one as "exterior, land and air," and one as "exterior, marine" are suggested.

D-1828. "Practice for Atmospheric Exposure of Adhesive-Bonded Joints and Structures." Whereas the three preceding standards utilize controlled laboratory conditions, this standard (a) defines classes of natural exposure and (b) outlines a weathering test practice for measuring strength loss as a function of time in those exposures. Several, somewhat extreme, natural environments and their associated geographic locations are mentioned.

D-1879. "Practice for Exposure of Adhesive Specimens to High-Energy Radiation." Specimens are exposed to controlled dosages of high energy radiation (x-ray, gamma, electron, or beta radiation, etc.) and changes in the before-and-after strengths noted.

D-2295 and D-2557. Procedures for measuring shear strength for metal joints at

low and high temperatures, respectively, on adhesive-bonded tensile lap shear specimens.

D-4299 and D-4300. Procedures for measuring the deteriorating effects of bacteria and molds, respectively, on joint strength (see details under durability testing for wood joints). Also useful for metal bonding adhesives which might be susceptible to molds or bacteria.

**Strength Under Exposure to a Hostile Environment.** Ideally, a durability test should measure an adhesive bond's retention of strength and bond *while exposed* to the elements of its service environment. However, the execution of such tests can be physically and procedurally quite difficult. The following two are D-14's only durability standards which are designed to test strength while joints are under exposure.

D-2918. "Practice for Determining Durability of Adhesive Joints Stressed in Peel" (Fig. 24). A dead load type test

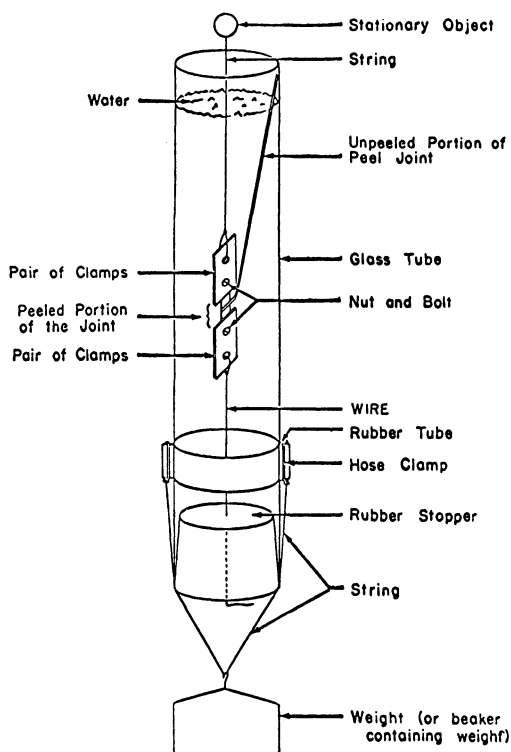


Fig. 24. Specimen and device for testing peel strength under environmental exposure (D-2918).

for the influence of water immersion on peel resistance. Several other standard environments are also suggested (i.e., various relative humidities, temperatures, salt spray, etc.).

D-2919. "Test Method for Determining Durability of Adhesive Joints Stressed in Shear by Tension Loading." Fig. 25 shows the lap shear specimen and spring-type loading device used. A number of standard environments are also suggested for use.

## Wood Bonding Adhesives

**Joint Strength Retained after Exposure to Accelerated Weathering Treatments.** Many of the durability testing concepts suggested for metal joints may also be useful with wood. One or more of the basic wood joint-strength tests (e.g., D-0897, D-0905, D-0906, etc.) could be combined with selected environmental exposure (D-0896, D-1151, D-1183, D-1828, D-4299, D-4300, etc.) to screen wood bonding adhesives for particular durability requirements.

In D-3024 (see wood adhesive specifications), samples of laminated wood and plywood are tested both before and after water exposure and variously evaluated for shear strength and/or wood failure. These procedures could have applications in other wood glue testing as well.

D-3110 (see wood adhesive specifications), tests for strength retained after exposure and sets forth minimum performance criteria. Exposures include atmospheric water soak, vacuum-pressure water soak, boiling, and exposure to elevated temperatures in an oven. Whenever dealing with adhesives falling in the categories covered by D-3110, durability should certainly be tested that way. However, these procedures almost certainly have other useful wood adhesive testing applications too.

In addition, D-3434, "Practice for Multiple-Cycle Accelerated Aging Test (Automatic Boil Test) for Exterior Wet Use Wood Adhesives" is available for those who have access to the rather complex and expensive apparatus involved. Often abbreviated as the ABT, it has produced very valuable wood adhesive durability data.

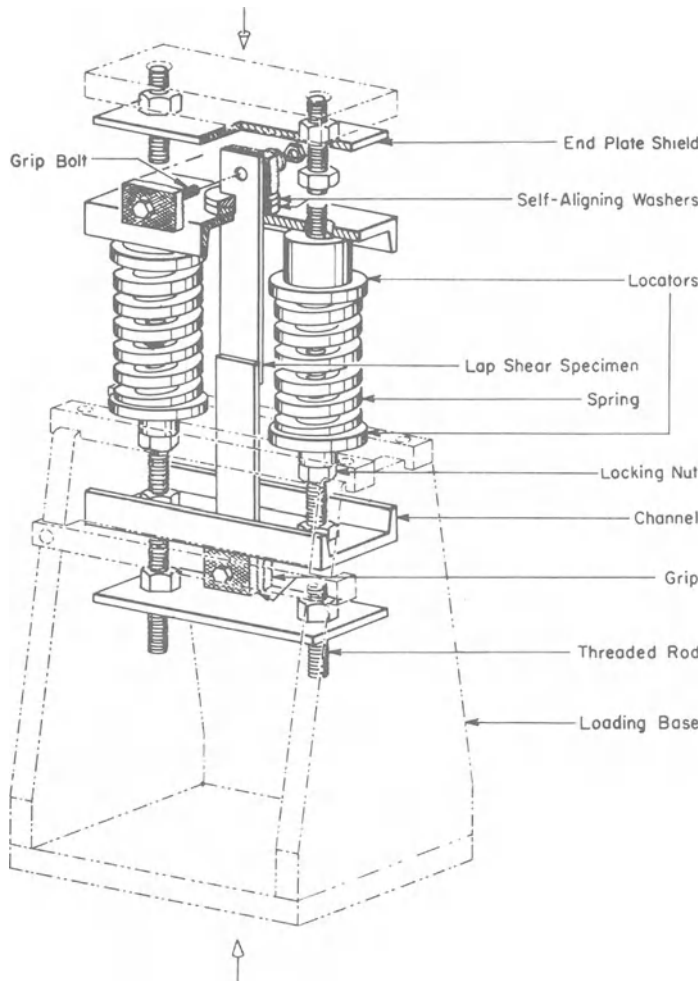


Fig. 25. Specimen and device for testing tension shear strength under environmental exposure (D-2919).

**Delamination of Wood Adhesive Bonds after Environmental Exposure.** Wood tends to shrink and swell as it is respectively dried and wetted during environmental exposure. As a result, significant stresses are imposed on the bonds and can result in delamination if the bonds are not properly formed using durable adhesives. Various cycles of wetting, drying, steaming, etc. are used in the D-14 standards which test for this property, and resultant percentages of glue-line delamination are measured. Several of these tests are from specifications, where maximum allowable delamination values are also given.

standard includes two delamination test procedures which are similar to but slightly different from the one in D-2559 (see below). Method A is a 3-day test, whereas Method B is a  $12\frac{1}{2}$  hour test used for daily quality control purposes in evaluating wood laminates.

D-2559 (on adhesives for exterior-use glued, laminated, wood) uses specimens cut from small laminated beams and tests for delamination after exposure to a multi-step accelerated aging treatment. See earlier listing under wood adhesive specifications.

D-1101. "Test Methods for Integrity of Glue Joints in Structural Laminated Wood Products for Exterior Use." This

**Rate Process Assessment of Heat and Moisture Resistance of Wood-Adhesive Joints.** D-4502, "Test Method for Heat and

Moisture Resistance of Wood-Adhesive Joints.” This recent standard defines procedures where the degrading effects of heat and moisture on bond quality are measured in such a way that the data can be analyzed by means of classical rate process equations. Results have shown that useful, long-term extrapolations of environmental effects can be made.

### Plastic and Glass Bonding Adhesives.

There are no D-14 standards specifically designed to test the durability of plastics or glass bonding adhesives. However, for screening purposes, one or more of the general-purpose adhesive strength tests could be combined with selected exposure and the associated strength loss measured.

For plastics, we do have the D-3929, “Practice for Evaluating the Stress Cracking of Plastics by Adhesives Using the Bent-Beam Method.” It recognizes that some adhesives may interact with plastic adherends in such a way as to induce areas of weakness leading to stress cracking.

With glass adherends, we can have the added problem of light penetrating a more or less transparent adherend, possibly having a photochemical effect on the adhesive, its interface, etc. Screening for this effect could be accomplished using a standard specimen (e.g., the D-4501 block shear) in combination with exposure to sunlight or to artificial light (e.g., D-0904).

### Paper Bonding Adhesives

Most standards for paper bonding adhesives are under the jurisdiction of TAPPI or related organizations. See ASTM’s two durability tests for paper bonding adhesives, D-1581 and D-1713 in the earlier listing under paper adhesive specifications.

## TESTING THE PHYSICAL AND WORKING PROPERTIES OF ADHESIVES

Although adhesives are screened predominantly on the basis of their strength and durability characteristics, there may be times when the testing of their physical, compositional and

working properties is also needed. These tests are relatively straight forward and are not discussed here but are listed in Appendix 2.

## Appendix 1

### Selected References of Use in Adhesives Familiarization, Selection, and Screening Testing

#### Computer Searchable Databases

“Standards and Specifications,” prepared by the National Standards Association, Inc., is available on line through the Dialog Information Retrieval Service, Palo Alto, CA. It references over 113,000 U.S. and International documents, including standards from ASTM, ANSI, the U.S. Federal Government and Military, and SAE, as well as others. In addition to information on the standard and its acceptance by ANSI and DOD, vendors of products and services conforming to the standard are given. Hard copy of many of the standards is also available from the National Standards Association.

“Standards Search,” prepared by ASTM and SAE, is available on line through the Orbit Search Service, McLean, VA. It contains over 15,000 references (some with abstracts) to the standards included in the ASTM Book of Standards and in the SAE’s Handbook, Aerospace Index, and Index of Aerospace Materials Specifications.

“Military and Federal Specifications and Standards,” prepared by Information Handling Services, is available on line through BRS Information Technologies, Latham, NY. Cites over 80,000 nonclassified U.S. Military and Federal standards and specifications, Joint Army-Navy specifications, Military Standard Drawings, and Qualified Product Lists.

“Combined Industry Standards and Military Specifications” is also prepared by Information Handling Services and available on line through BRS Information Technologies, Latham, NY. Cites over 150,000 government and industry standards. Covers some 50 U.S. and other national and international standards organizations, including the American National Standards Institute (ANSI), the International Standards Organization (ISO), and the National Bureau of Standards Voluntary Engineering Standards database, which is based on the standards of some 400 societies. Also includes the Military and related standards covered by “Military and Federal Specifications and Standards.”

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## Appendix 2

### Use-Oriented Classification of ASTM Adhesives Standards

#### Standard on Terminology of Adhesives

- D-907. "Terminology of Adhesives."

#### Standard Specifications for Adhesives

*For adhesives used in construction assembly bonding: primarily adhesives for tile or panel-to-frame bonding applications in building construction.*

- C-557. "Specification for Adhesives for Fastening Gypsum Wallboard to Wood Framing."
- D-1779. "Specification for Adhesive for Acoustical Materials."
- D-3498. "Specification for Adhesives for Field-Gluing Plywood to Lumber Framing for Floor Systems" (reference D-3632, "Practice for Accelerated Aging of Adhesive Joints by the Oxygen-Pressure Method" and D-3931, "Test Method for Determining Strength of Gap-Filling Adhesive Bonds in Shear by Compression Loading").
- D-3930. "Specification for Adhesives for Wood-Based Materials for Construction of Manufactured Homes."

*For primary wood bonding adhesives.*

- D-2559. "Specification for Adhesives for Structural Laminated Wood Products for Use Under Exterior (Wet Use) Exposure Conditions."
- D-3024. "Specification for Protein-Base Adhesives for Structural Laminated Wood Products for Use Under Interior (Dry Use) Exposure Conditions."
- D-3110. "Specification for Adhesives Used in Nonstructural Glued Lumber Products."
- D-4317. "Specification for Polyvinyl Acetate-Based Emulsion Adhesives."
- D-4689. "Specification for Adhesives, Casein-Type."
- D-4690. "Specification for Urea-Formaldehyde Resin Adhesives."

*For paper bonding adhesives.*

- D-1580. "Specification for Liquid Adhesives for Automatic Machine Labeling of Glass Bottles" (and com-

panion standard D-1584, "Test Method for Water Absorptiveness of Paper Labels").

- D-1874. "Specification for Water- or Solvent-Soluble Liquid Adhesives for Automatic Machine Sealing of Top Flaps of Fiberboard Shipping Cases" (and companion standard D-1714, "Test Method for Water Absorptiveness of Fiberboard Specimens for Adhesives").

*Pressure-sensitive tape specification.*

- D-1000. "Pressure-Sensitive Adhesive Coated Tapes Used for Electrical Insulation" (see ASTM Book of Standards, Part 10.01).

*Optical adhesive specification.*

- D-2851. "Specification for Liquid Optical Adhesive."

#### Strength Tests for Metal Bonding Adhesives

*Tensile strength of metal bonding adhesives.*

- D-0897. "Test Method for Tensile Properties of Adhesive Bonds."
- D-2095. "Test Method for Tensile Strength of Adhesives by Means of Bar and Rod Specimens" (and companion D-2094, "Practice for Preparation of Bar and Rod Specimens for Adhesion Tests").

*Shear strength of metal bonding adhesives.*

- D-1002. "Test Method for Strength Properties of Adhesives in Shear by Tension Loading (Metal-to-Metal)."
- D-2295. "Test Method for Strength Properties of Adhesives in Shear by Tension Loading at Elevated Temperatures (Metal-to-Metal)."
- D-2557. "Test Method for Strength Properties of Adhesives in Shear by Tension Loading in the Temperature Range from  $-267.8$  to  $-55^{\circ}\text{C}$  ( $-450$  to  $67^{\circ}\text{F}$ )."
- D-3165. "Test Method for Strength Properties of Adhesives in Shear by Tension Loading of Laminated Assemblies."
- D-3528. "Test Method for Strength Properties of Double Lap Shear Adhesive Joints by Tension Loading."
- D-3983. "Test Method for Measuring Strength and Shear Modulus of Nonrigid Adhesives by the Thick Adherend Tensile Lap Specimen."
- D-4027. "Test Method for Measuring Shear Properties of Structural Adhesives by the Modified-Rail Test."
- D-4501. "Test Method for Shear Strength of Adhesive Bonds Between Rigid Substrates by the Block-Shear Method."
- D-4562. "Test Method for Shear Strength of Adhesives Using Pin-and-Collar Specimen."
- E-0229. "Test Method for Shear Strength and Shear Modulus of Structural Adhesives."

*Bending strength of metal bonding adhesives.*

- D-1184. "Test Method for Flexural Strength of Adhesive Bonded Laminated Assemblies."

*Peel strength of metal bonding adhesives.*

- D-0903. "Test Method for Peel or Stripping Strength of Adhesive Bonds."
- D-1781. "Method for Climbing Drum Peel Test for Adhesives."

- D-1876. "Test Method for Peel Resistance of Adhesives (T-Peel Test)."
- D-3167. "Test Method for Floating Roller Peel Resistance of Adhesives."

*Cleavage strength of metal bonding adhesives.*

- D-1062. "Test Method for Cleavage Strength of Metal-to-Metal Adhesive Bonds."

*Impact strength of metal bonding adhesives.*

- D-0950. "Test Method for Impact Strength of Adhesive Bonds."

*Fatigue strength of metal bonding adhesives.*

- D-3166. "Test Method for Fatigue Properties of Adhesives in Shear by Tension Loading (Metal/Metal)."

*Creep of metal bonding adhesives.*

- D-1780. "Practice for Conducting Creep Tests of Metal-to-Metal Adhesives."
- D-2293. "Test Method for Creep Properties of Adhesives in Shear by Compression Loading (Metal-to-Metal)."
- D-2294. "Test Method for Creep Properties of Adhesives in Shear by Tension Loading (Metal-to-Metal)."

*Fracture strength of metal bonding adhesives.*

- D-3433. "Practice for Fracture Strength in Cleavage of Adhesives in Bonded Joints."

*Rate of strength development for metal bonding adhesives.*

- D-1144. "Practice for Determining Strength Development of Adhesive Bonds."

## Durability Tests for Metal Bonding Adhesives

- D-0896. "Test Method for Resistance of Adhesive Bonds to Chemical Reagents."
- D-0904. Light aging (see glass, durability).
- D-1151. "Test Method for Effect of Moisture and Temperature on Adhesive Bonds."
- D-1183. "Test Methods for Resistance of Adhesives to Cyclic Laboratory Aging Conditions."
- D-1828. "Practice for Atmospheric Exposure of Adhesive-Bonded Joints and Structures."
- D-1879. "Practice for Exposure of Adhesive Specimens to High-Energy Radiation."
- D-2295 and D-2557. Extreme temperature shear testing (see metal, strength, shear).
- D-2918. "Practice for Determining Durability of Adhesive Joints Stressed in Peel."
- D-2919. "Test Method for Determining Durability of Adhesive Joints Stressed in Shear by Tension Loading."
- D-3762. "Test Method for Adhesive-Bonded Surface Durability of Aluminum (Wedge Test)."
- D-4299 and D-4300. Mold and bacteria tests (see wood, durability).

## Standards on Preparation of Metal Surfaces for Adhesive Bonding

- D-2651. "Practice for Preparation of Metal Surfaces for Adhesive Bonding."

- D-2674. "Methods of Analysis of Sulfochromate Etch Solution Used in Surface Preparation of Aluminum."
- D-3933. "Practice for Preparation of Aluminum Surfaces for Structural Adhesives Bonding (Phosphoric Acid Anodizing)."

## Strength Tests for Wood Bonding Adhesives

*Tensile strength tests for wood bonding adhesives.*

- D-0897 and D-1344 (See metal, strength, tensile.)

*Shear strength tests for wood bonding adhesives.*

- D-0905. "Test Method for Strength Properties of Adhesive Bonds in Shear by Compression Loading."
- D-0906. "Test Method for Strength Properties of Adhesives in Plywood Type Construction in Shear by Tension Loading."
- D-1002. (See metal, strength, shear.)
- D-2339. "Test Method for Strength Properties of Adhesives in Two-Ply Wood Construction in Shear by Tension Loading."
- D-3528, D-4027, and E-0229. (See metal, strength, shear.)
- D-4688. "Test Methods for Evaluating Structural Adhesives for Fingerjointing Lumber."

*Bending strength test for wood bonding adhesives.*

- Not often used with wood adhesives, but D-1184 (see metal, strength, bending) should be applicable.

*Peel strength tests for wood bonding adhesives.*

- Not often used for wood but these standards should be applicable with wood as the rigid substrate: D-903, 180° peel; D-1781, climbing drum peel; and D-3167, floating roller peel (see metal, strength, peel).

*Cleavage strength test for wood bonding adhesives.*

- Not commonly done with wood adhesives but D-1062 (see metal, strength, cleavage) should be applicable with possible modifications to assure stressing the glue line.

*Impact test for wood bonding adhesives.*

- D-0950. "Test Method for Impact Strength of Adhesive Bonds."

*Fatigue strength test for wood bonding adhesives.*

- Not clearly applicable to wooden joints, but cyclic tension shear (e.g., D-1002) or bending (e.g., D-1184) test could be tried and strength examined as a function of number of cycles, percent of maximum load, etc.

*Creep tests for wood bonding adhesives.*

- D-3535. "Test Method for Resistance to Deformation Under Static Loading for Structural Wood Laminating Adhesives Used Under Exterior (Wet Use) Exposure Conditions."
- D-4680. "Test Method for Creep and Time to Failure of Adhesives in Static Shear by Compression Loading (Wood-to-Wood)."

- See also the creep test in D-3930 on adhesives for wood bonding in mobile homes.

*Rate of strength development for wood bonding adhesives.*

- D-1144. Procedure for rate of joint strength development (see metal, strength, miscellaneous).



## Durability Tests for Wood Bonding Adhesives

- D-0896, D-1151, D-1183, D-1828, D-2919. (See metal, durability.)
- D-1101. "Test Methods for Integrity of Glue Joints in Structural Laminated Wood Products for Exterior Use" (previously in ASTM Book of Standards, Part 4.09 on Wood but now to be in Part 15.06 on Adhesives).
- D-2559. "Specification for Adhesives for Structural Laminated Wood Products for Use Under Exterior (Wet Use) Exposure Conditions."
- D-3110. "Specification for Adhesives Used in Nonstructural Glued Lumber Products."
- D-3434. "Practice for Multiple-Cycle Accelerated Aging Test (Automatic Boil Test) for Exterior Wet Use Wood Adhesives."
- D-4299. "Test Methods for Effect of Bacterial Contamination on Permanence of Adhesive Preparations and Adhesive Films."
- D-4300. "Test Methods for Effect of Mold Contamination on Permanence of Adhesive Preparations and Adhesive Films."
- D-4502. "Test Method for Heat and Moisture Resistance of Wood-Adhesive Joints."

## Strength Tests Applicable to Plastics Bonding Adhesives

*Tensile strength tests for plastics bonding adhesives.*

D-1344 and D-2095. (See metal, strength, tensile.)

*Shear strength tests for plastics bonding adhesives.*

D-3163. "Test Method for Determining the Strength of Adhesively Bonded Rigid Plastic Lap-Shear Joints in Shear by Tension Loading."

D-3164. "Test Method for Determining the Strength of Adhesively Bonded Plastic Lap-Shear Sandwich Joints in Shear by Tension Loading."

D-3983. (See metal, strength, shear.)

D-4501. "Test Method for Shear Strength of Adhesive Bonds Between Rigid Substrates by the Block-Shear Method."

*Bending strength test for plastics bonding adhesives.*

D-1184. (See metal, strength, bending.)

*Peel strength tests for plastics bonding adhesives.*

Plastic films and rigid plastics could variously use the 180° peel (D-0903), climbing drum peel (D-1781) or floating roller peel (D-3167) (see metal, strength, peel).

*Cleavage strength test for plastics bonding adhesives.*

D-3807. "Test Method for Strength Properties of Adhesives in Cleavage Peel by Tension Loading (Engineering Plastics-to-Engineering Plastics)."

*Impact strength test for plastics bonding adhesives.*

Where applicable, perhaps use D-0950, the basic impact test.

*Fatigue strength test for plastics bonding adhesives.*

Where applicable, perhaps use a cyclic shear or bending test as suggested previously for fatigue testing of wood substrates.

*Creep tests for plastics bonding adhesives.*

Where applicable, perhaps use long term loading with the new block-shear test (D-4501) or consider the creep test methods now used for construction adhesives in the specification for adhesives used in bonding wood in mobile homes (D-3930).

*Miscellaneous tests for strength of plastics bonding adhesives.*

D-1144. Rate of joint strength development (see metal, strength, miscellaneous).

D-3808. "Practice for Qualitative Determination of Adhesion of Adhesives to Substrates by Spot Adhesion Test Method."

## Durability Tests for Plastics Bonding Adhesives

D-0896, D-1151, D-1183, D-1828, D-1879, D-2295, D-2557, D-2918 and D-2919. (See metal, durability.)

D-4299 and D-4300. Mold and bacteria tests (see wood, durability).

D-904. Light aging test (see glass, durability).

D-3929. "Practice for Evaluating the Stress Cracking of Plastics by Adhesives Using the Bent-Beam Method."

## Standard on Surface Preparation of Plastics for Adhesive Bonding

D-2093. "Practice for Preparation of Surfaces of Plastics Prior to Adhesive Bonding."

## Strength Tests for Glass Bonding Adhesives

*Tensile strength tests for glass bonding adhesives.*

D-0897 and D-1344. (See metal, strength, tensile.)

*Shear strength tests for glass bonding adhesives.*

D-3164. (See plastics, strength, shear.)

D-3658. "Practice for Determining the Torque Strength of Ultraviolet (UV) Light-Cured Glass/Metal Adhesive Joints."

D-4501. (See plastics, strength, shear.)

*Bending strength test for glass bonding adhesives.*

Probably not applicable.

*Peel strength tests for glass bonding adhesives.*

To test peel adhesion to glass as a rigid substrate, one could use the 180° peel (D-0903), climbing drum peel (D-1781) or floating roller peel (D-3167) tests.

*Cleavage strength test for glass bonding adhesives.*

Where applicable, perhaps use D-1062 with sandwich construction (see metal, strength, cleavage).

*Impact strength test for glass bonding adhesives.*

Where applicable perhaps use D-0950, the basic impact test method (see metal, strength, impact).

*Fatigue strength test for glass bonding adhesives.*

Where applicable, perhaps try D-3164 (tensile shear test for adhesively bonded plastic lap joints) with cyclic stressing.

*Creep test for glass bonding adhesives.*

Perhaps use D-2293 (see metals, strength, creep).

*Miscellaneous tests for glass bonding adhesives.*

D-1144. On rate of joint strength development (see metal, strength, miscellaneous).

D-3808. (See plastics, miscellaneous.) Spot adhesion test developed for plastics but may be usable with glass.

## Durability Tests for Glass Bonding Adhesives

D-0904. "Practice for Exposure of Adhesive Specimens to Artificial Light (Carbon-Arc Type) and Natural Light."

D-0896, D-1151, D-1183, D-1828, D-1879, D-2918, D-4299 and D-4300 (see metal, durability).

## Tests for Paper Bonding Adhesives

Most tests for paper bonding adhesives have been developed by TAPPI and published by them in "Testing Adhesives," by R. G. Meese (see Appendix 1).

*ASTM tests for strength of paper bonding adhesives.*

See tests in specifications D-1580 and D-1874 (under specifications, paper).

*ASTM tests for durability of paper bonding adhesives.*

D-1581. "Test Method for Bonding Permanency of Water- or Solvent-Soluble Liquid Adhesives for Labeling Glass Bottles."

D-1713. "Test Method for Bonding Permanency of Water- or Solvent-Soluble Liquid Adhesives for Automatic Machine Sealing Top Flaps of Fiberboard Specimens."

## Tests Relating to Other Specific Adhesives and Applications

D-0816. "Methods of Testing Rubber Cements" (see ASTM Book of Standards, Part 09.01).

D-2558. "Test Method for Evaluating Peel Strength of Shoe Sole-Attaching Adhesives."

## Tests Related to the Physical and Working Properties of Adhesives

*Tests for adhesive composition and chemical properties.*

D-1488. "Test Method for Amylaceous Matter in Adhesives."

D-1489. "Test Method for Nonvolatile Content of Aqueous Adhesives."

D-1490. "Test Method for Nonvolatile Content of Urea-Formaldehyde Resin Solutions."

D-1579. "Test Method for Filler Content of Phenol, Resorcinol, and Melamine Adhesives."

D-1582. "Test Method for Nonvolatile Content of Phenol, Resorcinol, and Melamine Adhesives."

D-1583. "Test Method for Hydrogen Ion Concentration of Dry Adhesive Films."

*Tests for applied adhesive weight.*

D-0898. "Test Method for Applied Weight per Unit Area of Dried Adhesive Solids."

D-0899. "Test Method for Applied Weight per Unit Area of Liquid Adhesive."

*Tests for rheological and tack properties of adhesives.*

D-1084. "Test Methods for Viscosity of Adhesives."

D-1146. "Test Method for Blocking Point of Potentially Adhesive Layers."

D-1875. "Test Method for Density of Adhesives in Fluid Form."

D-1916. "Test Method for Penetration of Adhesives."

D-2183. "Test Method for Flow Properties of Adhesives."

D-2556. "Test Method for Apparent Viscosity of Adhesives Having Shear-Rate-Dependent Flow Properties."

D-2979. "Test Method for Pressure-Sensitive Tack of Adhesives Using an Inverted Probe Machine."

D-3121. "Test Method for Tack of Pressure-Sensitive Adhesives by Rolling Ball."

D-4338. "Test Method for Flexibility Determination of Supported Adhesive Films by Mandrel Bend Test Method."

*Tests for properties of hot melt adhesives.*

D-3111. "Practice for Flexibility Determination of Hot Melt Adhesives by Mandrel Bend Test Method."

D-3932. "Practice for the Control of the Application of Structural Fasteners when Attached by Hot Melt Adhesives."

D-4497. "Test Method for Determining the Open Time of Hot Melt Adhesives (Manual Method)."

D-4498. "Test Method for Heat-Fail Temperature in Shear of Hot Melt Adhesives."

D-4499. "Test Method for Heat Stability of Hot-Melt Adhesives."

*Tests for electrical properties of adhesives.*

D-1304. "Methods of Testing Adhesives Relative to Their Use As Electrical Insulation."

D-2739. "Test Method for Volume Resistivity of Conductive Adhesives."

D-3482. "Practice for Determining Electrolytic Corrosion of Copper by Adhesives."

*Tests for working and storage life properties of adhesives.*

D-1337. "Test Method for Storage Life of Adhesives by Consistency and Bond Strength."

D-1338. "Test Method for Working Life of Liquid or Paste Adhesives by Consistency and Bond Strength."

D-1382. "Test Method for Susceptibility of Dry Adhesive Films to Attack by Roaches."

D-1383. "Test Method for Susceptibility of Dry Adhesive Films to Attack by Laboratory Rats."

*Miscellaneous adhesive properties tests.*

D-1916. "Test Method for Penetration of Adhesives."

D-3310. "Practice for Determining Corrosivity of Adhesive Materials."

D-4339. "Test Method for Determination of the Odor of Adhesives."

D-4500. "Test Method for Determining Grit, Lumps, or Undissolved Matter in Water-Borne Adhesives."

# Section B

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## Adhesive Materials

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## Animal Glue

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Animal glue has been used as an aqueous adhesive and size for thousands of years, and in more recent times has also found acceptance as a protective colloid, flocculant, and adhesive composition.

Commercial manufacture dates back to 1690 in Holland, 1700 in England, and the early 19th Century in the United States.<sup>1</sup> By 1900 there were at least 60 producers of animal glue in the United States; now there are only two.

Glue is derived from collagen, the major proteinaceous component of animal and fish skins, as well as tendons and the proteinaceous matrix of bones. In recent times the important commercial raw materials for making animal glue come from tanneries, which supply limed splits and chrome tanned pieces, and from slaughter houses, which furnish fleshings, hide pieces and bones.

The terms gelatin, technical gelatin, and animal glue refer to similar materials obtained from approximately the same stock but through different treatments. Edible gelatin and photographic gelatin are produced under more stringent conditions, producing a product of excellent color and clarity, low ash and low grease, combined with a very low bacteria count. These gelatins, because of manufacturing costs, sell for considerably more than technical gelatin and animal glues. Edible and photographic gelatins have tended to keep market share and have been the subject of continuing research.

Technical gelatin and animal glue, on the other hand, have seen their market share considerably eroded in the last 25 years. This decline has been brought about by the advent of synthetic polymers, which have taken over the sizing of synthetic fibers and the binding of paperback books. (But telephone books and catalogs have stayed with animal glue because of its superior durability and flexibility as well as lower cost.)

Because of the recent demise of a number of glue factories in the western world, there is currently a worldwide shortage of glue, particularly in the higher test grades. At this time there are only two manufacturers in the United States: Milligan & Higgins Division, Hudson Industries Corp., of Johnstown, New York, who make hide glue; and Swift Adhesives (Div. of Reichhold Chemicals), St. Joseph, Missouri, who make bone glue. Cattle are the major source, with rabbits and sheep contributing to a much lesser degree. A substantial amount of hide and bone glue is imported from Brazil, Chile, China, and other countries, and finds its way primarily into compounded adhesives and protective colloids. Leading importers of animal glue are Hudson Industries Corp., Olympic Adhesives, Inc., Nicholson & Co., Transatlantic By-Products Corp., and Swift Adhesives (Div. of Reichhold Chemicals).

It is estimated that domestic consumption of technical gelatin and animal glue is 25–30 million pounds per year.<sup>2</sup>

## CHEMISTRY

Animal glue is essentially the hydrolytic product of collagen, the main protein in animal skins and bones. Collagen as it exists in its natural state is water-insoluble and resistant to mild acids and alkalis as well as proteolytic enzymes other than the collagenases. Veis and Cohen discuss the structure of collagen:

A collagen fibril may thus be pictured as . . . segments varying in length and cross-section area due to differences in the cross-link distribution and the lateral ordering of the polypeptide chains . . . The segments are chain networks held together by sets of the acid-stable or B bonds. These segments contain and are held in the gross structure by the acid-labile A bonds and physical forces.<sup>3</sup>

The conversion of collagen to soluble polypeptides involves the breaking of covalent bonds and the disruption of physical forces through the use of either acid and heat or alkali and heat. Acid and heat cause selective disruption of some bonds plus selective peptide bond

hydrolysis, yielding tightly coiled lateral aggregates of peptide chains. Alkali and heat bring about a much more complete cross-linkage breakdown, resulting in randomly coiled peptide chains.

Veis<sup>3,4</sup> describes the collagen-gelatin transition as a stepwise process involving the melting of a trihelical network to an amorphous form, followed by the sequential hydrolysis of various types of covalent bonds.

Collagen from different species and even different parts of the same species varies in stability to acids, alkalis and heat because of differences in intramolecular and intermolecular organization. Glue molecules may be considered to be polypeptide chains containing amino acid sequences of varying lengths depending upon the treatment.<sup>5</sup> The amino acid analysis done by Eastoe, and corroborated by others, on an ox hide gelatin indicated that there are 18 separate amino acids present in varying amounts.<sup>6</sup>

Table 1 agrees within tolerable limits with that of Eastoe but also characterizes the ionic nature of the R-radicals on each amino acid.

**Table 1. Amino Acids in Animal Glue.<sup>5</sup>**

Amino Acid	Residues Per 1000 Total of All Residues	Character of R-Radical	
		Distinctive Groups	Ionic Character
Glycine	335.0	—	Neutral
Proline	128.0	Pyrrolidine in the chain	Neutral
Alanine	113.0	—	Neutral
Hydroxyproline	94.5	Hydroxypyrrolidine in the chain	Neutral
Glutamic acid	72.0	Carboxyl	Acid
Arginine	47.0	Guanido	Basic
Aspartic acid	46.5	Carboxyl	Acid
Serine	35.0	Hydroxyl	Neutral
Lysine	27.0	Amine	Basic
Leucine	23.0	—	Neutral
Valine	20.0	—	Neutral
Threonine	18.0	Hydroxyl	Neutral
Phenylalanine	13.0	Phenyl	Neutral
Isoleucine	12.0	—	Neutral
Methionine	5.0	Thiomethyl	Neutral
Hydroxylysine	5.0	Amine, Hydroxyl	Basic
Histidine	4.5	Imidazole	Basic
Tyrosine	4.4	p-Phenylene, Hydroxyl	Very weakly acid
Additional amino acids: <sup>7</sup>			
Glutamine	20	Primary Amide	Neutral
Asparagine	20	Primary Amide	Neutral

Later analyses of calfskin collagen<sup>7</sup> show two additional amino acid residues, glutamine and asparagine, each present in about 2% concentration (by number of residues). The distinctive groups have been added to the table.

Amino acid residues are amphoteric, containing both amine and carboxyl groups that are reactive and ionizable.

Amide groups may be hydrolyzed to carboxyl and amine by either alkaline treatment (leading to Type B gelatin) or extended acid degradation (Type A). This loss of amide groups and its relation to the isoionic point has been studied by Eastoe with the results shown in Table 2.

Because glues are amphoteric, they may react as cations or as anions depending upon the *pH* of the medium and the isoionic point of the glue. Prepared by the alkaline process, glues have a *pI* close to *pH* 4.8, while those processed in acid will have a *pI* near *pH* 9.0. The former react as cations, the latter as anions.

Gelation involves both intramolecular and intermolecular reorientation upon cooling the system. Veis,<sup>9</sup> among others, concludes that the collagen fold stability is influenced by solvent hydrogen bonding. A crystalloid structure is indicated. Gel formation involves the creation of random primary and secondary bonding; but intermolecular organization or network formations of gels is stabilized by secondary forces such as hydrogen bonding rather than primary covalent bonding. These bonds show a strong dependence upon solvent and temperature. Hydrogen bonding results in a sharp melting temperature whose value depends upon the number of these bonds that have formed.<sup>10</sup>

**Table 2. Relation Between *pI* and Amide Nitrogen.**

<i>Material</i>	<i>Treatment</i>	<i>pI</i>	<i>Amide Nitrogen</i> <sup>a</sup>
Calfskin	Unknown— Eastman Kodak	4.82	1.3
Hide	Lime	4.9	6.8
Hide	Lime	4.94	7.9
Calfskin	Lime and caustic	5.15	14.3
Ossein	Acid	7.8	35.6
Pigskin	Acid	9.4	43.7
Pigskin	Acid	9.4	42.9

<sup>a</sup>mmole/100 g protein

The intrinsic viscosity is a measure of the average volume occupied by the individual polymers molecules in dilute solution, where they are in their most random configuration.<sup>11</sup>

Stainsby<sup>12</sup> examined the viscosities of molecules of an alkali-processed gelatin at various *pH*'s. At the isoionic point in the absence of salt, the net charge on a glue molecule is zero and the molecule is in a compact form corresponding to its lowest viscosity in normal *pH* ranges. Alteration of the *pH* through the use of acid or base results in a net charge that will make the molecule either anionic or cationic. The ionic repulsive charges at these *pH* values prevent the chain from assuming a compact shape, thus causing higher viscosity. Subsequent additions of acid or alkali produce enough counter-ions to eventually neutralize the molecular repulsive charges, and the viscosity begins to collapse below *pH* 3 or above *pH* 10.

## MANUFACTURING

Animal glue is the water-soluble product of the hydrolytic degradation of water-insoluble collagen fibers. The products of hydrolysis vary greatly in molecular weight (approx. 10,000 to over 250,000), and measurements of viscosity and gel strength are necessarily average.

The approximate chemical composition of glue is:

Carbon	50.7%
Hydrogen	6.5%
Oxygen	24.9%
Nitrogen	17.9%

Only minor variations on the above composition are found in glues extracted from dissimilar stocks and different methods of manufacture.<sup>13</sup>

Glues in aqueous warm solutions undergo hydrolysis to lower molecular weights. The rate is dependent upon the *pH* and the temperature. The further the *pH* is from 7.0 in either direction, the more rapid will be the hydrolytic activity. Glue manufacturers recommend that dissolved glue solutions not be kept at temperatures above 140–150°F for extended periods, as this would cause thermal degradation.

Glues are subject to enzymatic as well as

bacterial attack. Particular care must be taken in manufacturing to reduce these effects through good manufacturing procedures and the use of preservatives. The preservatives currently preferred in the industry are phenols and phenol derivatives, zinc sulfate, and other types as indicated by particular industries.

The two categories of animal glue are hide glue and bone glue. *Hide glue* raw materials may include fleshings, limed or pickled splits, cattle pieces, and chrome-tanned hides and pieces. The producer of either hide glue or bone glue strives for greatest yield and cost efficiency, resulting in optimum test properties, including viscosity, gram strength (jelly), *pH*, moisture, foam, grease, ash, color, clarity, and odor.

Until very recently a high percentage of hide glue was derived from chrome-tanned skins. Reductions became necessary due to EPA constraints on chrome effluent. The tanning agent is largely removed by the application of caustic and then acid, after which the stock is washed. This process generally takes 24 hours. The stock is then soaked for a number of days in magnesium hydroxide and again washed, maintaining a slightly alkaline *pH*. The retention of a slight excess of magnesium hydroxide during the cook causes any remaining tanning agent in the skin to be precipitated as an insoluble hydroxide. The resulting glue is very light in color, almost transparent, with a grease content well below 1%.

A shorter method of chrome glue production uses much less water and greatly reduces the chemical effluent. Even though glue yields and tests are lower, this method tends to be cost-efficient in areas of high sewage rates. The method involves starting with a magnesium hydroxide soak as discussed and then cooking in the usual manner (in four steps as described below). The final product is similar to that obtained by the previous method, except for higher ash content ( $4\frac{1}{2}\%$  versus 3%).

Hide pieces and pickled splits as received must be thoroughly washed in cold water over a number of hours to remove salts, acids, offal, blood, etc. The stock is then soaked in cold milk of lime for a number of days or weeks, after which the lime is washed out. The *pH* is then adjusted with a small quantity of acid such

as hydrochloric, sulfuric, or phosphoric, which should completely permeate the swollen hide. The stock is next backwashed with water until the desired *pH* is reached. This could be 5–5.5 in order to obtain a *pH* of 6–7 in the finished product. Then the stock is transferred to cooking tubs containing perforated steam coils and water. The cook involves usually four extractions of approximately four hours each, at progressively higher temperatures. Drawdowns ranging from 2% to 9% glue solids are extracted and filtered. Finally, the glue liquor is evaporated to 20–50% solids, depending upon its viscosity.

In some countries glue continues to be dried in tunnel driers using heat and air which is passed over jelled sheets, stacked on wire nets with air spaces between. Modern driers feed jelled noodles, chips or beads on a continuous traveling screen through heat staged, filtered and conditioned hot air, until the moisture content is approximately 10–15%.

Limed splits may be placed in soaking vats directly for additional liming time, or processed as received depending upon the economics involved. It is cheapest to cook immediately, but the product has lower gram strength.

Fleshings, which contain as much grease as glue, are not a significant factor in domestic glue manufacturing at this time.

*Bone glues* are extracted from the collagenous matrix which is the chief organic constituent of all bone. Bone glues fall into two categories, extracted bone and green bone. Extracted bone glues are prepared from bones that have been solvent-extracted to remove by-product grease. Green bones are processed as received from slaughter houses. The bones are crushed, washed and processed in mild acid in pressure vessels. A series of extractions, alternating steam pressure in the jacket and sparging with hot water, removes the dilute glue liquor, which is then filtered or centrifuged to remove by-product grease. The glue is finally concentrated and dried. The residual bones are utilized as an additional by-product to produce bonemeal fertilizer, which contains approximately 85% calcium phosphate. Bone china derives its name from the fact that purified bone residue is incorporated into its manufacture.

## PROPERTIES

Dry animal glues are hard, nearly odorless materials ranging from pale yellow to dark amber. At approximately 260–270°C glue begins to decompose with swelling and charring, evolving dense smoke. Glue retains its characteristics unaltered if kept dry. Films heated above 100°C for relatively short periods become water resistant. Normal unmodified dry glue will absorb 6–8 times its weight of cold water, remaining in a jelled form until heated. The higher the test (viscosity/grams) the higher the melting point. An extremely useful property of aqueous glue solution is its ability to form a reversible gel upon cooling. This property can be modified to advantage by altering concentrations and/or adding modifiers.

The approximate specific gravity of glue is 1.27. The moisture content is normally 10–15%, ash 2.0–5.0%, pH 5.5–8.0, grease content 0.2%–3.0%.

Glues are soluble in water and insoluble in oils, waxes, organic solvents and absolute alcohol, but emulsification can be achieved in both water-oil and oil-water systems. Glue emulsions serve as encapsulating agents.

Glues can be precipitated in the laboratory by absolute alcohol, tannic acid, picric acid, phosphotungstic acid, or a saturated solution of zinc sulfate. Aluminum, ferric, chromic, and magnesium sulfate thicken, coagulate, or precipitate glue from solution; mild tannage and melting point increases can be achieved with the proper use of these compounds.

Numerous patents have been granted for systems involving the insolubilization (cross-linking, tanning) of glue. Formaldehyde and aldehyde donors are effective.

Glue gives a positive reaction to the biuret test and also Molisch's test. In the absence of other nitrogen containing materials, the percentage of glue is, by commercial agreement, the Kjeldahl nitrogen multiplied by the factor 6.25.

Dried films deposited from solutions are continuous, resilient, and noncrystalline, and develop shear tensile strength in excess of 3000 psi on glue-bonded wooden blocks; indeed, tensile strengths as high as 10,000 psi have been reported for glue films.<sup>14</sup>

Glue can be modified by a variety of chemical reactions, including acetylation of the hydroxyl groups, alcoholysis to yield amino acid esters, and aryl sulfonation to give complexes insoluble in water but soluble in organic solvent. Reaction with fatty amines improves water resistance. Quaternization yields cationic molecules. The literature abounds with ideas for modification.<sup>15</sup>

Animal glue has been compounded with many materials, e.g., starches, dextrans, sugars, various salts, sulfonated oils, emulsions of oils, polyvinyl alcohol, polyvinyl acetate; plasticizers such as glycols, glycerine, and sorbitol; as well as some water-soluble organic solvents such as butylcarbitol acetate. Viscosities can be modified by compounding with compatible natural gums, alginates, and synthetic thickeners such as carboxymethylcellulose.

Glue manufactured by an acid process, whose *pI* is approximately 9.0, possesses a jelly strength-to-viscosity ratio of 4–5:1; while alkaline-treated glue whose *pI* is approximately 4.8 has a ratio of  $2\frac{1}{2}$ –3:1.

The melting point of glue and glue compositions can be varied from below room temperature to over 120°F by altering the test of the glue, changing the glue-water ratio, and the addition of specific chemicals. Viscosities are controlled by glue strength, glue-water ratio, total solids, and temperature; glues have good working characteristics from water-thin to approximately 70,000 cps.

## TEST GRADES

Animal glue manufacturers grade their production according to gram strength or jelly strength, which increases with viscosity. Peter Cooper Corp., one of the earliest and largest manufacturers of animal glue and gelatin in the United States, developed the grading system about 1844. Procedures and equipment evolved over the years and did not become standardized until well into the 20th Century.

Table 3 cross references the now closed Peter Cooper's code designation with that of Milligan & Higgins. This table takes into consideration only alkaline-extracted glue, which



**Table 3. Glue Test Grades (Hide Glues).**

<i>Peter Cooper Standard Grade</i>	<i>Milligan &amp; Higgins Standard Grade</i>	<i>Bloom Grams</i>		<i>Millipoise Value (Minimum)</i>
		<i>Range</i>	<i>Mid-Point</i>	
5A Extra	8A	495-529	512	191
4A Extra	6A	461-494	477	175
3A Extra	5A	428-460	444	157
2A Extra	4A	395-427	411	145
A Extra	2A	363-394	379	131
#1 Extra	A	331-362	347	121
# 1 Extra Special	X	299-330	315	111
# 1	2XA	267-298	283	101
1XM	2X	237-266	251	92
1X	3XA	207-236	222	82
1 $\frac{1}{4}$	3X	178-206	192	72
1 $\frac{3}{8}$	4X	150-177	164	62
1 $\frac{1}{2}$	5X	122-149	135	57
1 $\frac{5}{8}$	6X	95-121	108	52
1 $\frac{3}{4}$	7X	70-94	82	42

accounts for the greatest proportion of hide glue production.

Bone glues differ from hide glues in method of extraction, and have smaller ranges of jell strength and viscosity. The gram strength-viscosity ratio is quite different, particularly in the medium to high test range where bone glues tend to have higher ratios of gram strength-to-viscosity, on the order of 4:1. (Swift bone glue seems to be an exception, with ratios closer to those of hide glue.) In addition, bone glues tend to have slightly lower pH values (5.5) than hide glue (6.3).

The price of glue increases with test grade. The higher the test grade, the higher the glue's viscosity, water absorption, and melting point, the faster it sets to a gel, the more aggressive the tack, and the stronger the dried film.

## TESTING

The viscosity in millipoise is determined by the flow time in seconds through a standard pipette of a 12.5% solution of the glue at 60°C.

To determine the jelly value, the 12.5% solution is first chilled at 10°C for 16-18 hours. Then the gram strength is obtained by the use of a Bloom Gelometer or comparable instrumentation which measures the force necessary to move a 0.5 inch diameter plunger (resting on the surface of the jell) a distance of 4 mm at prefixed speed.

The solution pH is measured at 40°C. Mois-

ture content, relative foam value, ash content, and grease content are also of concern.

## CUSTOMER PREPARATION OF GLUE SOLUTIONS

The glue manufacturer often feels frustrated because some customers have inadequate mixing equipment and/or housekeeping problems. Although glues contain bacterial inhibitors the situation can get out of control if the equipment is not clean, and fresh glue solution is continually run in on the remains of older batches.

Glues are available in 10, 20, or 30 mesh granulation. The glue is dissolved in water preheated to 150-170°F, in an agitated stainless steel vessel which has been cleaned to avoid bacterial contamination from earlier batches. Concentration ranges from 5% to 50%. Large batches are usually processed in jacketed vessels either using electrically heated oil jackets or vented water jackets with low pressure steam injection. Smaller vessels usually have electrically heated oil jackets or low wattage electrical elements placed directly on the vessel surface. Agitation is important for rapid and uniform dissolving of animal glue and its compounded forms. Agitators of various types and speeds are used depending upon the type of industry, the viscosity of the solution, and the need to keep foam levels within required limits.

## LIQUID ANIMAL GLUES

Liquid animal glues are glues modified by gel depressants so that they remain fluid somewhat below room temperature. Urea, thiourea, and ammonium thiocyanate are the usual gel depressants, incorporated at approximately 8–20% by weight of the total formula. The ability of this product to stay fluid with normal temperature reduction allows for very slow assembly time, an important characteristic in the furniture industry. The final bond is achieved as the water is slowly removed from the glue, increasing its concentration and tack, thus overcoming the gel depressant effect, then setting and finally drying. The resulting film has high tensile strength. Further modifications can be obtained by the addition of materials such as clay, calcium carbonate, plasticizers, wetting agents, etc. Formulations may range between 35% and 65% solids with viscosities of 3000–5000 cps at room temperature.

## FLEXIBLE AND NON-WARP GLUES

Flexible and non-warp glues are compounded animal glues containing modifiers such as sucrose, corn syrup, dextrin, clay, acid, salt, magnesium sulfate, glycerine, glycols, sorbitol, water soluble organic solvents, surfactants, perfume, and preservatives; in the case of cake glue, water is added.

Because of differences in equipment, application, and end product, the cake glue is tailored for each user, and further alterations to the formula may even be made to compensate for seasonal changes in temperature and humidity. Properties of importance include viscosity at a particular running temperature (e.g., 135–155°F), speed and degree of tack, and bonding characteristics. Glues supplied as cakes have the advantage of easy meltdown and may be added directly to the applicator pans.

Flexible glues are used primarily in book binding, including telephone directories, also in soft luggage and other products where a permanently flexible, strong, resilient adhesive film is desired. A good flex product contains approximately two parts glue to one part plasticizer. The higher test glues employ more plasticizer to maintain a desired flexibility.

Glue test can vary from 135 to 450 gram strength.

Non-warp glues do not have good flexibility, but can possess fairly good “lay flat” characteristics through the addition of sugars. They can be compounded to yield very strong dry films. The major areas of use are in the paper box trade in hand fed, semiautomatic and automatic covering machines, in the application of cover stock in the book manufacturing industry, in hard notebook binders, phonograph record covers, hard luggage, etc.

Dry non-warp glues are very similar to non-warp cake glue except that the manufacturer supplies this product as a dry fine mesh material which the customer must dissolve in hot water prior to use. Advantages are indefinite shelf life and lower shipping cost because of the absence of water.

A dry, moderately flexible glue, patented by M. Konigsberg, contains 8–20% glycerine but remains free-flowing indefinitely. The method utilizes the absorptive properties of synthetic alkaline earth metal silicates such as hydrous calcium silicates (e.g., Micro-cel, Johns-Manville) and other specially prepared synthetic silicas.<sup>16</sup> It has met with considerable success in the bookbinding industry.

Viscosity measurements are made by Brookfield viscosimeter or Zahn cup. Readings of solids content, as a means of monitoring viscosity and water loss, can be made by refractometer. Manufacturers of glues and compounds can supply customers with viscosity/solids and viscosity/temperature graphs.

## GLUE APPLICATION

Cake glue, compounded dry glue, and straight dry glue are utilized at temperatures between 135 and 155°F (57 and 68°C). Too low a temperature does not allow for good wetting and filling of the pores of the substrate before the glue sets, resulting in bond failure. Temperatures that are too high create prolonged open time, with resultant slower productivity. Elevated temperatures also result in high moisture loss in the reservoir and heat hydrolysis, resulting in weaker glue strength. Dry glues are usually prepared at 25–55% solids, depending upon the test glue used, the speed of production

necessary and the type of material to be bonded. It is bad practice to dilute high test glue in order to retard gelation. This practice can result in a "starved" glue bond or insufficient dry glue to perform the job. Instead, gel depressants can be added. The materials to be glued must be neither too hot nor too cold. Additional heat to the system can slow adhesion, while a cold substrate can cause premature gelling with poor bonding.

The woodworking industry observes four time-honored steps:

1. Deposit a thin continuous glue film on the surface to be bonded.
2. Permit the glue film to become slightly tacky before mating surfaces and applying pressure.
3. Apply uniform pressure.
4. Continue pressure to insure initial bond strength.

Since it is applied from aqueous solutions, animal glue is not a filler, and only performs well as an intimate thin film in combining. The relationship of viscosity to concentration and test value is shown in Table 4.

Mating porous surfaces requires a heavier bodied (higher solids) glue, while thinner bodied glue is indicated for dense, nonporous surfaces.

## COATED ABRASIVES

At the present time the largest consumer of animal hide glue is the abrasives industry. Abrasives are involved in the enormous production

of wood products and the fine finishes essential to machinery, automobiles, household equipment, and appliances.

There are two principal classifications of coated abrasives:

1. Sandpapers and sand cloths in rolls, sheets, bolts, disks, cones, and other specialties.
2. Set up abrasive wheels, belts, disks, cones, and bobs, generally prepared in the user's own plant for grinding and buffing of metal, plastic, and wooden items.

In the production of coated abrasives there are five basic steps:

1. The backing material is presized, if necessary, with low test glue or glue/starch blends. This loading at approximately 35–40% solids imparts body and strength.
2. The presized cloth or paper is fed through a glue applicator which deposits the making coat in the film thickness dictated by grit size. The larger the grit size, the thicker the glue laid down. The making coat takes full advantage of the jelling characteristic of glue. The glue concentration can be 25–45% and may be loaded with extenders such as calcium carbonate. The glue grades vary with the application and the type of grit. The higher grade glues are used for silicon carbide and aluminum oxide, the medium grades for emery and garnet, the lower grades for flint.
3. The grit is uniformly dispersed upon the

**Table 4. Viscosity in Centipoises at 140°F for Dry Glues of Given Grade Test and Millipoise Value.<sup>17</sup>**

<i>Glue % Concentration</i>	<i>High Test (155 m.p.)</i>	<i>Medium High Test (102 m.p.)</i>	<i>Medium Test (63 m.p.)</i>	<i>Low Test (32 m.p.)</i>
5	3.0	2.4	2.0	1.6
10	8.8	5.6	3.6	2.6
12.5	15.5	10.2	6.3	3.2
15	28.0	17.2	8.4	5.0
20	79.2	46.0	22.4	10.0
25	196	112	49.6	19.6
30	524	264	108	37.6
35	1360	612	224	72.0
40	3216	1320	476	133
50	16320	7240	2400	566

unjelled glue film through a gravity feed hopper. The grit can be electrostatically oriented in the vertical position until the glue is jelled, by which time the product is partially dried.

4. A thin film of animal glue, and in some cases a resin, is laid down over the grit, further locking it into the adhesive matrix.
5. The abrasive cloth or paper is fed to a carefully controlled hot air drier. It is then wound into jumbo rolls for storage and later cut into various shapes.

### SET-UP WHEELS

Under the heading of set-up polishing wheels are abrasive wheels, belts, disks, and bobs. The user prepares these on site by laying down a making coat and applying a particular grit. In some instances the grit is top coated with a more dilute glue and then carefully dried. Glues of various test values are utilized as dictated by the severity of the end use. Applications include metal finishing, glass grinding, granite finishing, and grinding in the leather industry.

### GREASELESS BUFFING COMPOUNDS

Greaseless abrasive compositions are manufactured as sticks, finding a considerable market as abrasive compounds for recoating cloth buffing wheels used for metal finishing. The stick is held against a revolving wheel where the heat of friction melts the compound, transferring it to the wheel. A layer of grit compound is deposited which contains approximately 6–8% high test glue, 24% water, and the remainder, abrasive grains.

Of particular importance in these sticks is shelf life. Considerable attention must be paid to chemical preservation, guarding against bacterial breakdown which would lead to soft, non-performing sticks.

### GUMMED TAPE

Both low test hide glue and bone glue have played an important role in the manufacture of gummed tape. Glue has to a certain extent been replaced by dextrin or combined with dextrin

to lower cost. Glue is ideal for gummed tape because of its fast, aggressive tack, rapid set, permanent bond and excellent machinability. The open time, tack, set time, wetability, and strength of bond are often altered, depending upon the end use, by varying the glue test or adding modifiers such as dextrin, wetting agents, jell depressants, and plasticizers.

Formulations usually have around 50% solids. The adhesive weight per square foot varies over a wide range, but typically the dry glue solids amount to 25% of the weight of the paper.

In the manufacture of gummed tape, large rolls of paper are fed through a glue applicator, where the adhesive at a temperature of 140–145°F is applied by the use of pick-up rolls. The tape is passed under tension over drying rolls or through a drying tunnel, then stored as jumbo rolls until slit and cut into standard sizes for the trade.

### GLASS CHIPPING

A unique application of glue has been perfected in the process of glass chipping. This procedure involves pouring warm glue solutions onto clean glass and allowing the glue to dry. As the film dries it shrinks and has a predisposition to curl. Since the dry glue is stronger than the glass and the bond formed with the glass is tenacious, the glass chips, leaving a rather uniform, floral like design. Lower test glue leads to a finer, more evenly chipped texture. Patterns and lettering can be formed by appropriately covering areas of the glass with metal foil prior to introducing the glue.

### SIZING AND COATING

Glue as a size has been used to advantage for many years in the textile industry, particularly on cotton, rayon, acetate and viscose. The newer man-made fibers such as nylon, orlon, and Dynel have in some instances been successfully warpsized with animal glue. Compositions containing 2.5–8% glue solids are suitable. Various test grades of glue are utilized depending upon the application. For maximum stiffness, unmodified glues are used. Usually, however, the glue is modified with plasticizers

and softening agents such as glycerine, sorbitol, sugars, sulfonated oils, and wax emulsions. The size composition usually contains 20–45% lubricants and softening agents.

In the process of weaving crepe the yarns used are held in a tight twist by glue while being woven into fabric. Later the glue is washed out during boil-off, thus releasing the twist and creating a creping or pebbled effect.

Another use is in warp sizing, where the objective is to strengthen and coat the yarn to be woven. The glue composition acts as a lubricant and a protective coating on the yarn to prevent breakage and chafing. The composition is later washed out preparatory to finishing and dyeing.

## PAPER

Animal glue has played an important role in the manufacture of papers and paper products. The important attributes of glue, including film formation, colloidal properties, and amphoteric nature, have led to its being used as a sizing agent, protective colloid, colloidal reagent, and adhesive.

Glue is a protective colloid for rosin particles during beater sizing, particularly when hard water is encountered. In practice the glue is added near the end of the beater operation. The paper fiber, with a  $pH$  of 4.5 or less, is positively charged in relation to the glue, whose charge is negative. The glue/rosin is therefore attracted to and held by the paper fiber. The addition of small quantities of glue improves the internal sizing, toughness, density, formation erasability, and resistance to scuffing of the final product.

Glue improves the wet strength of paper and can later be insolubilized, or it may be incorporated with resins that are aldehyde donors under certain conditions, rendering the glue water resistant. Glue as a surface size on papers such as fine writing paper, currency, and blue-print stock imparts strength, tear resistance, folding qualities, moisture resistance, and soil resistance and prevents feathering of inks.

For tissue paper made with a Yankee drier, glue or a combination of glue and polyvinyl alcohol is well established as an aid. Small

amounts of glue or glue combinations are incorporated into the wet paper stock, creating a very slightly tacky film at the drier surface which prevents blowing or lifting to the doctor blade as it is peeled off the drum.

The process of making paper with the Fourdrinier machine or paper board with cylinder machines involves the use of modified animal glue as a colloidal flocculant. Incorporated with the fine cellulose fibers may be fillers, pigments, colors, and rosin. By adjustment of the  $pH$  of the system with acids, alkalies or salts, the amphoteric nature of the glue may be changed to a highly charged negative or positive colloid. The effective reaction of 0.5–1.0% glue solution on the system is that of flocculation, resulting in enhanced water drainage and paper formation. Normal usage rates are approximately two pounds of glue per ton of paper.

The same type of glue solutions are also employed in the Saveall process for recovery of solids by agglomeration in the effluent white waters of paper mills.

## COMPOUNDED RUBBER

Relatively large amounts of glue form the basis for the successful use of compounded synthetic rubber in textile mills. The accepted practice of maintaining heat and humidity in textile mills creates problems of fiber lapping, i.e., winding around the drafting roll during operation. The addition of approximately 25–50% glue by weight to compounded synthetic rubber produces cots and aprons with a very significantly diminished tendency to lap as long as humidity is present. This reaction is explained by the reduction of the electrokinetic or zeta potential between the rubber and moisture to near zero by the incorporation of an electrolyte such as glue. The zeta potential of approximately zero at the rubber-moisture interface of the system (fiber-moisture-moisture-rubber) effectively prevents lapping.<sup>18</sup>

## GASKET MANUFACTURING

Gaskets have long been made from selected paper products of various thickness and density

impregnated with animal glue. The object is to produce a gasket that is water and solvent resistant, flexible, compressible, resistant to distortion, and easily cut, one that provides a tight seal and will not fuse to the body.

The process involves the saturation of the paper stock by floating it across a tank containing a glue/plasticizer solution, then passing through squeeze-rolls to remove excess liquid. In a second pass, the wet impregnated paper is moved through a bath of curing agent and (optional) plasticizer. The paper is then dried and later cut into shapes. The final product is flexible, waterproof, etc. Variables include paper type and thickness, glue test, and formula modifiers.

## MATCHES

The match industry consumes animal glue in the manufacturing of "strike-anywhere," book matches, and wooden safety matches. Glues of various tests and foam characteristics are specially formulated. The glue acts as a binder for the ignition chemicals, combustible fillers, and inert materials and is also an important contributing factor in the formation of a head of correct density, form, and strength.

Match glues possess rigidly controlled grease content, usually below 0.3% on dry weight of glue. By careful blending, specific foam characteristics can be obtained. These are described as foam height, in mm, and foam half-life, or the time in minutes for half the foam to dissipate. The foam creates a uniform porous head which contains oxygen to promote the ignition and combustion.

## METAL REFINING

Electrolytic metal refining for gold, silver, copper, antimony, and lead is improved with animal glue. Without glue as a modifier in the electrolytic bath, the disposition of the metal at the cathode becomes coarse, with the formation of nodules. These can be eliminated by inclusion of 0.03–0.15% glue in the bath, resulting in a finer particle disposition with the absence of nodules. Some refiners request that the glue not be defoamed so that it can create

a blanket of foam on the bath suppressing the evolution of fumes.

## OTHER APPLICATIONS FOR ANIMAL GLUE

Technical gelatin (high quality animal glue) of relatively low test is being used successfully in microencapsulation. The gelatin can be used to encapsulate many materials as long as the latter do not react with or invade the thin film of gelatin surrounding them.

Carbonless paper uses the technique of gelatin encapsulation of ink, whereby the application of pressure ruptures the gelatin microspheres, releasing ink to a copy.

In the manufacture of printer's rollers, glue is compounded with glycerine/sorbitol, water, and a curing agent such as hexamine to produce a tough, flexible, resilient, water resistant, smooth roller with a long life. The roller is used in the printing industry to transfer ink to the impression plate. Glues for this purpose are in the 350–450 gram range.

Medium-to-low test unfoamed glue is utilized in the production of strong, cellular, lightweight concrete.

Technical gelatins are also employed in the manufacture of protein hydrolysates, an ingredient in personal care items such as skin creams, hair shampoos, and cosmetics. Generally the gelatin is reduced to a molecular weight under 2000 by the use of enzymes or caustic and further combined chemically at reactive sites to form modified proteins of interest to the industry.

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# Casein and Mixed Protein Adhesives

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The casein, soy protein, and blood adhesives are often considered as a family of adhesives because they have some properties in common. Although similar, the chemical structures of these three proteins are different enough to give unique properties to the adhesives which are made from each. This chapter will primarily cover the casein adhesives, but will touch also on some of the properties common to the three protein sources and the use of combinations of casein-soy, casein-blood, and casein-soy-blood in the same adhesive. In the matter of terminology, *casein adhesive* will be used as a broad term embracing all the adhesives based on casein; but for the casein-lime-sodium salt wood glue, the colloquial term *casein glue* will be used.

## HISTORY

The use of casein and animal blood as adhesives goes back over many centuries, while the use of soybean flour and other soy products for adhesives and binders is a recent development in view of its long history as a food. Both casein and animal blood owe their place in adhesive history to the water-resistant formulations which have been made from them.

*Casein* is the main protein of milk. Salzberg<sup>1</sup> notes that the adhesive nature of the casein curd was recognized in ancient Egypt. It has been identified as the glue in ancient museum pieces and in wood backs and frames holding price-

less paintings of the Renaissance. Early use required only mixing of the wet curd with lime. Casein was supplied for glue in Switzerland and Germany in the early 1800s. A century later mixtures of dry casein, lime, and sodium salts were patented, the first of the convenient commercial dry mixed casein glues, which are added to water at the time of use. For several decades casein was the preferred wood glue for furniture and plywood—wherever a measure of water resistance was needed. But casein gave way to phenolic resin adhesives (1931–1935), urea formaldehyde resin adhesives (1937), resorcinol resin adhesives (1943), and water resistant polyvinyl acetate copolymers (in the 1970s). Polyvinyl acetate emulsion adhesives (in the 1960s) became a popular choice where water resistance was not important. Despite this strong competition, there is still a steady and substantial market for casein, as wood glue, protective colloid, paper pigment binder, foil laminating agent, label paste adhesive, etc.

*Animal blood* also has old credentials. According to Lambuth,<sup>2</sup> there is evidence that the Aztec Indians, the ancient people of the Mediterranean, and the people of the Baltic used blood as a water resistant structural adhesive. There was an increase in the use of blood as an adhesive in the period from 1910 to 1925, following the discovery of a method for producing dried soluble blood. This use coincided with the need for water-resistant plywood for the airplane industry in World War I. Heat-cured



blood glues were the most water-resistant plywood adhesives available at that time and remained so until the development of phenol-formaldehyde resin film glues in the early 1930s. Blood glues are covered in detail by Lambuth in Chapter 11 of the second edition of this Handbook.<sup>2</sup>

*Soybean flour* first came into use as an adhesive in the 1920s, when a method was developed for extracting the oil from the soybean meal without altering the solubility of the protein. Soybean flour was widely used as a wood adhesive before World War II. It is still an important adhesive in many phases of the wood utilization industry, with much of its use in combination with casein or blood or both (see Lambuth<sup>3</sup> in Chapter 10 of the second edition of this Handbook).

## CASEIN AS A RAW MATERIAL

### Current Market Position of Casein

All of the casein used in the United States is imported. This product has not been manufactured in this country since the early 1950s when the U.S. dairy producers switched production to non-fat dry milk. This followed the passage of the dairy price support program in 1949, whereby the price of non-fat dry milk was supported while that of casein was not. In the 1980s industrial users in the United States have been working with the Committee to Assure the Availability of Casein (C.A.A.C.)<sup>4</sup> to inform Congress of the significant contribution of casein to this country's economy, in an attempt to counter the drive by the dairy lobby to impose tariffs and restrictions on the importation of casein. The industrial users of casein have shown that their use of casein in no way infringes on the sale of dairy products.

In 1985 and 1986 the casein sources which played a significant role in the adhesive industries were New Zealand, Australia, France, Ireland, Uruguay, Russia, and Poland. Argentina, one of the major suppliers to the adhesive industry in the 1960s and 1970s, has cut its casein production to the point that Argentine casein comprised less than 1% of the casein imports in 1985, and none in 1986 and 1987.<sup>5</sup>

The recent cost of casein to the consumer has risen from an average of 90 cents per pound in

1985 to as high as \$2.50–2.75 per pound in late 1988, with a premium for casein meeting special specifications. The cost abated somewhat by the second quarter of 1989.

### Manufacture of Casein

Commercial casein is obtained from cow's milk, in which it is the main protein at about 3% concentration. Most of the casein for adhesives is obtained by acid precipitation; however, some is precipitated from milk by rennet, a preparation made from the stomach of young calves. Only the use of acid casein is covered here, since a very limited amount of rennet casein is used for adhesives.

Acid casein is manufactured by a selective precipitation process. Skim milk is prewarmed to 42–45°C and acidified with dilute acid. The acid may be hydrochloric or sulfuric, or it may be provided by the addition to the milk of a bacterial culture which produces lactic acid from the lactose. According to Spellacy,<sup>6</sup> in some parts of the world sour whey which has been permitted to obtain an acidity of approximately 1–2% lactic acid by natural fermentation is used as the precipitating agent. After precipitation, the steps followed in the manufacturing process are: draining off the whey, washing and pressing the curd, and finally, drying and grinding the casein.<sup>7</sup> Historically, lactic casein has been the type used for adhesives. However, the purity and quality of the product depend more on the structure of the curd and the thoroughness with which it is washed than on the type of acid used. In the last decade all three types of casein—lactic, sulfuric, and hydrochloric—have been available for adhesives.

### Specifications and Typical Analyses for Casein

There are no universal specifications for casein as a raw material. Each manufacturing country has its own way of grading its product, usually based on purity, cleanliness, and solubility. A high quality casein is one which has a high protein, and a low free acidity, total acidity, ash, fat, and lactose, indicating a product prepared under closely controlled conditions. It is low in insoluble material such as overdried casein par-

**Table 1. Typical Analyses, Industrial Casein Used in the United States.<sup>8</sup>**

	<i>High Grade</i>	<i>Medium Grade</i>	<i>Low Grade</i>
Moisture, %	9-13	8-12	8-12
Ash (unfixed), %	0.75-1.8	1.2-2.0	2.0-2.7
Protein (N $\times$ 6.38), %	83-88	83-86	82-84
Free acidity, (as % lactic acid)	0.1, max.	0.2-0.7	0.9-1.8
pH value	4.0-5.5	4.0-5.0	4.0-5.0
Dirt content (mg per 100 grams)	0.5-3.0	2-7	8-14
Insolubles (ml per 100 grams)	0.1-0.6	1-2	2-20
Viscosity (15% solids, NH <sub>4</sub> OH solution), cp	900-1200	800-1200	700-1000

ticles or other protein fractions of the milk. It is clean and free of dirt or other extraneous material which can contaminate the casein during the manufacturing, grinding, or packaging process. It has a creamy white appearance, the clean odor of fresh milk, and a low bacterial and fungal count.

The high quality casein described above is not necessary for all industrial adhesives. The important features for many adhesives are minimal viscosity variations and predictable performance in a formula. For some applications the particle size is important, and either the normal 30 mesh casein is specified, or for many processes not using heat for solubility, a 60 or an 80 mesh. Tables 1 and 2 give typical analyses for the industrial casein currently in use in this country.<sup>8</sup> Standard methods for testing casein appear in the "Encyclopedia of Industrial Chemical Analysis," Vol. 9, 1970,<sup>9</sup> and in TAPPI Monograph 35, 1974.<sup>10</sup>

Casein is listed as "generally recognized as safe" (GRAS) in the Code of Federal Regulations (CFR), Title 21, Part 182.90, April 1, 1979, covering substances migrating to food from paper and paperboard products. CFR, Ti-

tle 21, Part 175.105, April 1, 1977, covering adhesives regulated by the Food and Drug Administration, states that these regulated adhesives may contain substances classified as GRAS, subject to the stated limitations of 175.105.<sup>11</sup>

## CHEMISTRY AND PHYSICAL PROPERTIES OF GLOBULAR PROTEINS

Casein, soy, and blood are globular proteins, soluble in water or aqueous acids, bases, or salts. The molecules are spherical in shape and made up of heavily coiled (folded) chains of amino acids, whose side chains are cross-linked.<sup>13</sup> Because of hydrogen bonding with each other, the highly polar reactive groups of the amino acids are not available until after a dispersion process, which is usually an alkaline treatment. The usefulness of this group of proteins as adhesives is based on their high degree of polarity in the dispersed state.

Proteins are amphoteric. In neutral solution both the basic and carboxyl groups are generally charged, corresponding to the dipolar ions of the amino acids. At the isoelectric point dissociation as an acid is equal to that as a base, so that solubility and rate of migration in an electric field is at a minimum.<sup>14</sup>

Proteins are also extremely prone to undergo some form of alteration, described as *denaturation*. Lambuth has described in some depth the effect of denaturing agents on blood and soy protein in Refs. 2 and 3. Many of his explanations apply to casein as well, and will be covered in the section on formulation of casein glues.

*Soy protein* differs from casein in structure, as shown by Coco and Scacciaferro.<sup>15</sup> In the

**Table 2. Typical Sieve Analyses on Casein,<sup>12</sup> Percent (Cumulative)**

	<i>30 M (all in)</i>	<i>30 M</i>	<i>60 M</i>	<i>80 M</i>
On 20 Mesh	0.1	0	—	—
On 30 Mesh	0.5	6.0	0	—
On 50 Mesh	60.0	72.0	10.0	0
On 70 Mesh				1.5
On 80 Mesh	86.0	92.0	73.2	8.9
On 100 Mesh	91.0	95.0	87.2	30.9
On 200 Mesh	97.0	98.0	98.0	80.4
Passing 200 Mesh	3.0	2.0	2.0	19.6

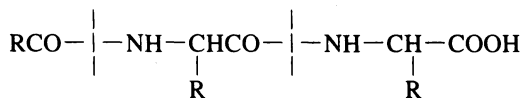
soy molecule, much of the hydrophobic region is enclosed within the hydrophilic region, so that many of the polar groups are unavailable. In casein, the hydrophobic and the hydrophilic regions are at opposite ends of the coiled chain, and the polar groups are more accessible. Coco and Scacciaferro have been able to restructure the soy molecule by thermochemical means to make more polar groups available. They showed that casein can be 90% solubilized at a pH of 6.5 but this solubility remains unchanged even if the pH is increased to 12. With the unmodified soy protein, on the other hand, the solubility shows a gradual climb, from 60% at pH 6 to 88% at pH 11.5.

The dried blood product which is used for the protein blend adhesives is the *soluble blood* type, which is 80–95% soluble in water. This product becomes strongly adhesive in alkaline dispersed form at a lower pH than the soy product.

### CHEMICAL PROPERTIES OF CASEIN

Casein exists in milk as the calcium salt, and is classified as a *phosphoprotein*. It is thought that the phosphoric acid is esterified with the hydroxyl groups of the lysine chains of the protein. Precipitation of casein by the enzyme *rennet* leaves organically bound phosphate, while *acid precipitation* causes the casein to split off the calcium phosphate. The ash content of rennet casein is high, about 7%, reflecting the presence of the calcium salt, while that of acid casein is relatively low, about 2%, with a small amount of calcium phosphate as an impurity.<sup>16</sup>

The protein structure of the casein molecule was described by Salzberg et al.<sup>17</sup> to consist of chainlike compounds united through the peptide linkage where R may be  $-\text{H}$ ,  $-\text{CH}_3$ ,  $-\text{C}_6\text{H}_5$ ,  $-(\text{CH}_2)_4\text{NH}_2$ ,  $-\text{CH}_2\text{COOH}$ , etc.:



Ref. 17. Reprinted with permission.

Casein will dissolve in basic solutions. These solutions can be dried down yielding a soluble salt, e.g., sodium, potassium, or ammonium caseinate. The caseinate in solution will chelate

**Table 3. Amino Acid Composition of Casein, Wt. %.<sup>18,19</sup>**

<i>Hydrophilic, ionizable, acidic</i>	
glutamic acid	22.4
aspartic acid	7.1
tyrosine	6.3
<i>Hydrophilic, ionizable, basic</i>	
lysine	8.2
arginine	4.1
histidine	3.1
<i>Hydrophilic, non-ionizable</i>	
proline	10.6
serine	6.3
threonine	4.9
methionine	2.8
tryptophan	1.2
<i>Hydrophobic</i>	
leucine	9.2
valine	7.2
isoleucine	6.1
phenylalanine	5.0
alanine	3.2
<i>Sulfur bridge</i>	
cystine	0.34
<i>Unclassified</i>	
glycine	2.0

heavy metal ions, such as calcium, aluminum, or zinc. The chelating mechanism is pH dependent—the higher the pH, the greater the chelating capacity. Reaction with metals whose salts are relatively insoluble gives water resistance to the casein.

The amino acid composition of casein is shown in Table 3. This breakdown was reported in 1949 and 1950 by Gordon and co-workers.<sup>18</sup> The classification of the amino acids into the hydrophilic and hydrophobic groups and subgroups was taken from a visual representation of the amino acids and side groups of the casein molecule by N. King.<sup>19</sup>

### PHYSICAL PROPERTIES OF CASEIN<sup>20,21</sup>

Casein is a granular solid, varying in color from cream to light yellow, typically having a sweet and milky odor. Poorly prepared casein may have a deeper yellow color and at times a rancid or musty odor. The moisture content of casein usually falls between 8 and 11%, but it is

not unusual to see ranges from 7 to 13%. Casein is insoluble in water and most non-aqueous media, but it forms colloidal dispersions in aqueous solutions of acids, bases, and some salts. Some organic substances can also disperse casein. The ones having practical applications are urea and the thiocyanates. (Although the term *dispersion* is technically the correct one when referring to casein treated in a manner to break the internal hydrogen bonding, uncoiling the molecule, the term *solution* is more frequently used. The two terms will be employed interchangeably in this discussion.) Casein is insoluble at its isoelectric point,  $pH$  4.6. Although it has minimal solubility around this point, any success preparing solutions at  $pH$ 's close to the isoelectric point require very careful control of conditions. There is a marked increase in solubility below  $pH$  3 and above  $pH$  6. There is little application for acidic casein solutions (those prepared at  $pH$ 's below 3.0) and they are seldom used for industrial purposes. Basic solutions are typically prepared in the 7–9  $pH$  range at concentrations of from 10 to 20%, and show Newtonian properties. At concentrations greater than 18% most solutions are too viscous to be handled conveniently at 25°C. Casein solutions at 25% solids, prepared with most bases, are jellies at 25°C.

Urea can be used to disperse casein at a  $pH$  of 5.5 to 6.0. It can also be used to obtain a higher solids content, since it has a thinning effect. Basic solutions are highly receptive to

additional water, while urea-cut solutions have minimal water acceptance. Dried films of basic solutions are soluble in water, but the dried films of urea solutions will not dissolve easily unless the  $pH$  is raised by addition of a base. Addition of aldehydes and heavy metal ions increases the viscosity and water resistance of casein solutions. Dicyandiamide, used in a basic solution, is a very effective viscosity reducer, and generally reduces the water resistance. The viscosity-temperature and viscosity-concentration relationships are exponential. Salzberg<sup>22</sup> reported this relationship between viscosity and concentration, showing values in centipoises of 1080, 26,000, and 160,000 for 15, 20, and 25% concentrations, respectively. At 25°C a 20% concentration solution may hardly flow, but it will be free-flowing at 60°C. The variables which affect the apparent viscosity of casein solutions are: concentration, temperature,  $pH$ , type of cation, age, and method of preparation—especially the time, temperature, and order-of-addition factors. The complex relationship of the viscosity, type of cation, and  $pH$  factors was reported by Salzberg et al.<sup>23</sup> and is shown in Table 4.

#### Other Viscosity Factors

The viscosity of the raw casein and its reactive potential upon exposure to metal ions directly affect the viscosity of casein adhesives and solutions. The inherent viscosity depends on sev-

**Table 4. Viscosity of Casein Solutions Prepared with Different Alkalies at Varying  $pH$ 's.<sup>a,b,25</sup>**

Alkali Added	$pH$						
	6	7	8	9	10	11	12
Sodium hydroxide (NaOH)	300	700	900	1000	900	300	100
Ammonium hydroxide (28.6% $NH_4OH$ )	—	900	1000	1300	1000	1000	—
Sodium carbonate ( $Na_2CO_3$ )	—	1400	1700	2400	3600	—	—
Trisodium phosphate ( $Na_3PO_4 \cdot 12H_2O$ )	800	1200	3200	5700	8000	10300	—
Borax ( $Na_2B_4O_7 \cdot 10H_2O$ )	700	800	1300	3700	—	—	—

Source: Ref. 10. Reprinted with permission.

<sup>a</sup>In centipoises measured at room temperature.

<sup>b</sup>Casein concentration 14% by weight.

eral factors: the season of the year as it relates to the lactational cycle of the herd, the genetic makeup of the herd, and the protein content and the purity of the casein. The casein produced from milk obtained early season, shortly after the calving, will be twice as high in viscosity as that produced in late season. Creamer<sup>24</sup> determined that in a controlled test, high pH and high calcium content of the casein will result in a higher viscosity product. Countries which have poor manufacturing facilities frequently lack control over the temperature and pH of precipitation, and have inadequate washing cycles. This results in a high ash, high acidity, low protein casein, containing a higher percentage of milk by-products. These caseins are lower in viscosity and less reactive in formulations which use metal ions for added water resistance. The viscosity difference between these poorer quality caseins and those manufactured under modern and controlled conditions shows up more sharply when they are tested in a higher solids urea solution at a pH below 7. It is essential, when testing a casein lot for suitability, that the viscosity be determined by running the test within the structure of the formula which is to be used, and with the intended dispersant and crosslinking chemicals.

### LIME-FREE CASEIN ADHESIVES

Casein is utilized in diverse ways, as an adhesive, as a binder, and as a protective colloid and stabilizer for emulsified adhesive systems. Casein is sold as a raw material, and casein adhesives are sold in both the dry and liquid forms. The useful wood adhesive known as casein glue, which is formulated with lime and sodium salts, will be addressed later. This section will cover other uses of casein, for which the solubilization of the casein is generally accomplished with the use of heat, and at lower pH's than for the lime-containing glues.

#### Preparation of Casein Solutions, General

When given sufficient time, casein can be solubilized cold with most alkalies and alkaline salts, but cold solubilization usually results in a lower viscosity product with very little stability. Most of the lime-free casein adhesives

are prepared with heat because of many advantages, the most important of these being the ability to speed up and control the process, and to result in a uniform and stable product. Urea has widespread use as a dispersant for casein and is discussed in the section on label paste adhesives. Selection of one or a combination of two or more dispersants, is determined by many factors relating to the intended use of the solution, pH range desired, and other agents used in the system. Table 5<sup>26</sup> shows the percent of various alkalies needed to solubilize casein.

Ammonium hydroxide is the most commonly used alkali. It is generally added in excess of the amount necessary for solubilization, because frequently some of the ammonia volatilizes in the cooking process; also, excess ammonia has a preserving effect. Frequently ammonia is used in combination with borax, improving the preserving properties of each. Studies have shown that although a casein solution made with borax has good biocidal properties, at a pH of 6.9 it does not equal the adhesive and viscosity properties in storage of a solution made with 5% borax plus 10% ammonium hydroxide, which has a pH of 9–10.<sup>27</sup> Ammonium hydroxide has also proven useful for pH adjustment at the end of the cooking period. Except for sodium hydroxide, ammonia-cut casein solutions are lower in viscosity than those cut with other alkalies. Borax imparts a very high viscosity to a casein solution, and when it is used alone at 12% on the casein weight, most of the caseins on today's market will dissolve at a pH of about 7.0.

Sodium hydroxide is a strong base and should be used in small amounts, just enough to achieve solubility, the amount needed varying with different caseins. Generally 2.0–2.5% will be sufficient to solubilize the casein and will result in a pH of 7. The amount of alkali needed varies with different caseins, so should be worked out in each instance. Table 4<sup>28</sup> shows the effect of pH on the viscosity of casein solutions prepared with several alkalies. Note that at pH 9, sodium hydroxide and ammonium hydroxide cut solutions are at their peak viscosity, but when alkaline salts are used, the viscosity increases continuously as the percent salt increases. The sharp drop-off in viscosity of the solutions cut with sodium hydroxide at

**Table 5. Typical Alkalies Needed to Dissolve Casein, and pH Values of Casein Solutions.<sup>a,26</sup>**

<i>Alkali Added</i>	<i>Alkali, Parts per 100 parts of Casein, by Wt.</i>							
	2.5	5.0	7.5	10	12.5	15	17.5	20
NaOH	7.0	11.0	12.6	—	—	—	—	—
NH <sub>4</sub> OH (26°Be)	7.7	9.2	10.0	10.3	10.6	10.7	10.8	—
Na <sub>2</sub> CO <sub>3</sub>	—	6.7	7.4	8.3	9.1	9.7	10.0	10.2
Na <sub>3</sub> PO <sub>4</sub> · 12H <sub>2</sub> O	—	—	—	6.8	7.2	7.4	7.7	7.9
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> · 10H <sub>2</sub> O	—	—	—	6.8	7.3	7.7	7.9	8.1

Source: Ref. 10, Reprinted with permission.

<sup>a</sup>In centipoises measured at room temperature.

pH's above 10 is also of special interest. Potassium hydroxide behaves in a similar manner, with the sharp drop in viscosity coming between pH 10.8 and 11.

### Preservatives

Casein, as a milk product, is susceptible to microbial attack, and requires protection with an appropriate biocide when the product containing it is to be kept in the liquid form more than a day. The level of biocide should not be based only on the casein present, but should be calculated to be effective in the total system of which the casein is a part. Sodium orthophenylphenate and sodium pentachlorophenate have a long history as effective preservatives for casein products. Less harsh preservatives are the esters of *p*-hydroxybenzoic acid. Other useful ones are chlorinated methylisothiazolin, tributyltin oxide, and chlorinated xlenols. Formaldehyde is effective, but its use is a concern for OSHA, and it also causes viscosity increases because of its strong crosslinking tendency with casein. It must be handled very carefully when used with casein. Many new biocides are now available due to recent advances in biological protection. An appropriate one should be selected after considering the use of the end product, the environmental impact of disposal of waste, and applicable governmental regulations.

### Preparation of an Alkaline Casein Solution

A formula and the steps in the preparation of a 15% alkaline dispersed casein solution is given

below:

#### Parts by weight

Casein	100
H <sub>2</sub> O	555
NH <sub>4</sub> OH (26°Be)	9
Biocide	*

\*Follow the manufacturer's recommendation for level of selected biocide and guidelines on point and method of introduction.

(1) Using continuous agitation during the preparation, charge the water into a jacketed kettle. Add the casein and allow to soak for 10 minutes to wet the grains of casein thoroughly. (2) Warm the casein-water slurry to approximately 43–49°C. (3) Add the NH<sub>4</sub>OH and continue heating until reaching 60°C, holding at this temperature for 20 minutes or until solubilization is achieved. (4) Cool to 49°C. Most biocides are added at this point. If the aim is to prepare a solution with long term stability, extend the solubilization period from 20 minutes to 30, and increase the temperature during solubilization to 71°C. (The extra time and temperature is necessary to destroy the proteolytic enzymes, which could cause viscosity to drift down, or sometimes up, during the storage life of a casein solution. Enzymatic breakdown of casein can occur in solutions which are adequately protected with biocide, so this is an additional problem to be addressed.)

### Additives for Casein Solutions<sup>29</sup>

For many purposes the formula and procedure would be modified. A casein solution quite often is high in viscosity and foamy. A casein

film is brittle and adsorbs water easily. A number of additives have been used. *Antifoams and defoamers* include amyl alcohol, silicone oils and emulsions, octyl alcohol, tributyl citrate, pine oil, and tributyl phosphate. Frequently used *viscosity reducers* are urea, dicyandiamide, and ammonium thiocyanate. The *plasticizers* may be divided into true plasticizers, which dissolve in the polymer, and flexibilizing agents, such as the resins and latexes which do not dissolve, but merely form a blend of the two components, acting as a softening agent. Plasticizers used for casein are glycerol, sorbitol, latex, glycols, urea, sulfonated oils, water, and resin emulsions. The *hardeners to increase moisture resistance* are formaldehyde, urea-formaldehyde resin, aluminum formate, hexamethylenetetramine, melamine-formaldehyde resin, lime, glyoxal, zinc salts and oxides, and alum.

## APPLICATIONS USING CASEIN SOLUTIONS AND ADHESIVES

### Casein as a Protective Colloid<sup>30,31,32</sup>

Casein is used widely as a stabilizer and protective colloid in latex systems. Ref. 31 gives formulas for use of ammonium caseinate as a stabilizer in a number of latex dipping operations—with neoprene latex to make neoprene gloves and a metal coating compound; with natural latex to make toy balloons, footwear, canvas work gloves, high modulus drug sundries, and flexible squeeze toys; and with natural latex to make latex molded products. Ammonium caseinate is used with styrene butadiene (SBR) to make a dry combining adhesive, tile adhesive, and rug, upholstery and linoleum backing; and with natural latex to make shoe adhesives. Potassium and sodium caseinates are also sometimes employed. When used to stabilize latex, the percent caseinate solids needed will vary with different latexes, but in all instances caseinate will increase the viscosity.

Casein is also suitable as a stabilizer in resin emulsions, and as a thickener for anionic emulsions. On occasion, the resin emulsions are used as tackifiers for the latex systems. The amount of casein needed for stabilizing a resin

emulsion must be balanced against the undesired loss in water resistance and tack when too much casein is used. These applications are covered in further detail elsewhere in this volume, particularly in the chapter on tackifying resins and natural and synthetic rubbers.

Success in stabilizing a resin with casein is dependent on following the proper procedure when combining the materials. Levels of various components are given in parts by weight. The resin (40–43) is dissolved in toluene (10–14) in the presence of oleic acid (0.25–0.75). Resins can be blended, or toluene may be increased to achieve the desired viscosity of 25–30 poises and an optimum particle size. The potassium oleate plus the caseinate provide a versatile emulsifier system which delays the break of the emulsion. Then, potassium hydroxide (0.15–0.2) in a 2.0–2.5% solution is added slowly to form potassium oleate in situ, followed by ammonium caseinate (1.3–1.5), added as a 10–15% caseinate solution. When an ester type resin is used, the caseinate is prepared with a low level of ammonium hydroxide. To this point there is a high viscosity *water-in-oil emulsion*. Then, there is a second addition of potassium hydroxide (a diluted KOH/water premix) equal to the first, triggering an inversion to a low viscosity *oil-in-water emulsion*, which has a small particle size and is very stable. The resin emulsion may then be compounded with a latex to produce an emulsion adhesive. When the resin is a hydrocarbon type, the total solids are generally 45.7–50.0%, and the pH is 10.3–10.7.

### Paper Coatings

Casein and isolated soy protein are the two protein binders used by the paper coating industry. They are normally used in combination with one of the latexes, styrene-butadiene, butadiene-acrylonitrile, or acrylic emulsions. Casein and isolated soy dispersions are usually compatible with each other; however, in practice, they are not generally combined in the same formula. The casein coatings show a better gloss and strength than the soy coatings. A soy protein coating is thixotropic, and a casein coating Newtonian, although these properties may be affected by the use of latex and the

preparation process. The thixotropy of the soy coatings gives them the advantage of running better on high speed coaters. Because of difficulties in completely dispersing the isolated soy protein at a low *pH*, the preparation of a casein cook is simpler than that of a soy protein cook. Due to the high *pH* necessary for dispersion, frequently, the soy protein cooks must be acidified after solubilization to bring the *pH* down. For prevention of flocculation of the pigment when the casein or protein solution is added, the pigment is generally alkalized first, and the first portion of the solution is added slowly. Sometimes casein is combined with starch as a binder for coatings for paper board and carton stock. When starch is cooked with casein, the temperature of the cook must be high enough to cook the starch. Generally 71°C is adequate, and this temperature is acceptable for casein.

The amount of binder (casein, soy protein, or latex) for a paper coating is given in dry parts of binder per 100 dry parts of clay. Usually 16–20% binder is used, and the ratio of casein (or soy protein) to latex is varied to give desired properties to the coating. Since excessive shear on the latex results in foam and possible physical breakdown, the latex should be added after the casein. When the latex is styrene-butadiene (SBR), an increase in casein and a decrease in SBR results in a higher viscosity at a lower solids. The reverse effect is used to advantage in preparing coatings: the latex-to-casein ratio is increased in order to accommodate a higher percent solids. At higher solids, heavier coating weights may be applied. The use of different latexes and different latex/casein ratios will result in different viscosities, rheology, and tack. SBR latex adds desirable properties to pigmented coatings bound with casein, improving the gloss, the varnish holdout, and the water resistance.<sup>33</sup>

A comprehensive discussion of the use of casein and isolated soy protein in paper coatings may be found in Tappi Monograph Series No. 22.<sup>34</sup>

Table 6<sup>35</sup> shows typical paper coating formulations with a 50 : 50 SBR-to-casein ratio, for use on two types of coaters. For a multiple roll coater, water would be added to adjust to a percent total solids of 50–55, giving a coating weight of 3–4 lb per 1000 sq ft. For an air knife

**Table 6. Casein/Latex Paper Coating.**<sup>35</sup>

	Parts by Wt	
	Dry	Wet
Pigment		
Coating grade clay	94.0	134.2
TiO <sub>2</sub> (rutile type)	6.0	8.6
Binder		
SBR latex	8.0	16.7
Casein	8.0	53.3
Water	(Sufficient to yield desired % solids)	

Source: Ref. 33. reprinted with permission.

coater, solids would be adjusted to 40–45%, yielding a coating weight of 2–3 lb per sq ft.

A typical formula for a casein cook is shown in Table 7<sup>36</sup>, with choices of alkalies given. Due to the volatility of ammonia and in order to assure complete solubilization of the casein when ammonia is used, Salzberg et al. recommended dissolving casein to a predetermined *pH* value. The preparation steps are the same as given earlier for an alkaline casein solution, except that the 60°C temperature is recommended for solubilization. The practice of dropping the casein solution into a clean storage tank and rinsing out the kettle between batches or at least once a day should be followed.

### Foil-to-Paper Laminating Adhesives

One of the better known uses of casein is the manufacture of foil-to-paper laminating adhesives. Because of its listing as GRAS by the FDA, casein is used for much of the packaging in the food and cigarette industries.

**Table 7. Typical Mill Formula, Low Solids Casein Solution.**<sup>36</sup>

Water	365 gal in clean jacketed kettle
Casein	500 lb
NaOH	16.25 lb, or
NH <sub>4</sub> OH(26°Be)	5 gal, or
Na <sub>2</sub> CO <sub>3</sub>	60 lb, or
Borax	75 lb
Yield	414.25 gal
Casein solids	14%, air dry basis
Casein per gal	1.2 lb.
Viscosity at 80°F	1000–3000cp
<i>pH</i>	8.0–8.4

Source: Ref. 17. Reprinted with permission.



A typical foil adhesive is made by first preparing an ammonium caseinate solution with a low level of ammonium hydroxide, and then combining it with a styrene-butadiene (SBR) latex with a *pH* of about 7.0. The *pH* of the resulting adhesive should be close to neutral because of the tendency of high *pH* adhesives to slowly eat through the foil. Some proprietary formulations at *pH*'s below 7 contain additives to increase water resistance. To make a simple casein-latex foil laminating adhesive: (1) Dissolve 20 parts of casein in 78.75 parts of water, using 1.25 parts of  $\text{NH}_4\text{OH}$  (26°Be) as the dispersant. (2) Combine 16 parts of this 20% ammonium caseinate solution with 52 parts of SBR latex. (3) Add two parts of defoamer as needed, one of a sulfonated wetting agent, and 0.5 of preservative. (4) Add water to a total formula weight of 100. The SBR should be non-carboxylated with 25–50% styrene, with rosin acid as the protective colloid.

#### Ice Water Label Paste Adhesives

Ice water label paste is a very specialized water-based casein adhesive which is used primarily to adhere paper labels to beer bottles. The labels must remain attached if the bottles are chilled in ice or otherwise subjected to wet conditions, but they must wash off reusable bottles easily with hot water. Casein is dispersed with urea at an approximate 50 : 50 ratio in the presence of ammonium hydroxide as an additional dispersant. The high percent casein solids in this type formulation is possible because of the urea, which acts as a viscosity reducer. The urea, sometimes along with ammonium thiocyanate, functions also as a gel depressant. Zinc oxide and zinc acetate are used to cross-link and provide water resistance. A defoamer and a preservative are always included. Starch is one of several agents incorporated to shorten the thread of the adhesive to improve its performance on high speed labelling machines.

Because the formulas in commercial use are proprietary, the one given in Table 8 gives typical ranges, not specific percentages. The compounding of the components is of equal importance to the formula. A successful order of addition must be established, along with a time-temperature log which relates to both the

**Table 8. Typical Label Paste Formula.**

	<i>Parts by weight</i>
Water	47–50
Preservative	0.3–0.5
Defoamer	0.5
Starch	1.5–3
Zinc acetate	0.3–0.5
Zinc oxide <sup>a</sup>	0.5–0.75
Urea (micropilled)	21–23
Casein	20–25
Ammonium hydroxide (26°Be)	1.0–1.6

<sup>a</sup>Zinc oxide is usually added as a 50% dispersion

points of introduction of the various raw materials and the heat-up, cook, and cool-down periods. A recommended order of addition for the formula given is:  $\text{H}_2\text{O}$ , zinc oxide, zinc acetate, preservative, defoamer, starch, urea, casein, and ammonium hydroxide. It has been established that for the primary components, use of the order: ammonium hydroxide, urea, and casein, gives a very unstable product, which tends to increase in viscosity sharply for several days, and then to drop off just as sharply. The typical cook temperature is 77–80°C. This temperature is held for 15–20 minutes before initiating the cool-down period.

A small formula change can make a large change in properties. Increased zinc oxide will give faster drying, but will shorten shelf life. Usually, to get a faster drying time, the gel depressant is decreased and the casein is increased, but a shift in this direction will shorten the shelf life. A very short shelf life is known in the industry as *setback*, and is a major problem when it occurs. The experienced formulator balances the formula to gain the best compromise in properties. A successful label paste must also meet the special running conditions of the machines which apply the labels at a fast speed. Various grades of casein, and even different lots within a grade, may perform differently. It is helpful to use a test for the selection of casein which relates to the formula in which it is to be used.

Specifications for viscosity, speed of set, and water resistance vary with the consumer. Table 9 gives the typical ranges for the properties desired in a label paste.

**Table 9. Typical Specifications for Ice Water Label Paste.**

Viscosity	45,000–75,000 cp @ 80°F (27°C)
Solids	48–50%
pH	7.5–8.5
Setting time	Fiber tear in 30 seconds
Water resistance	Pass 24 hr soak in water @35°F (2°C) <sup>a</sup>
Shelf life	3–6 months <sup>b</sup>

<sup>a</sup>Label is adhered to bottle and is dried for 24 hours before soaking.

Label must not flag off the bottle following 24 hr soak.

<sup>b</sup>The shelf life must hold at a stable viscosity with no sharp climb or drop for this period of time.

### Miscellaneous Uses for Casein Adhesives

A casein-lime adhesive and other casein based adhesives are involved in a cone winding process bonding paper to paper. The cones are used by the textile mills as yarn carriers. There are some specialty manufacturers of stable casein solutions who sell their products for varied applications.

A casein coating on steel is one step in the manufacture of aperture masks for color TV tubes.<sup>37</sup> Casein is also used as a partial binder in some types of caulking adhesives.

### CASEIN AND PROTEIN BLEND GLUES AS WOOD ADHESIVES

The wood adhesives discussed here will be the casein-lime-sodium salt glues and similar glues formulated with combinations of casein with soy flour, blood, or both. The pH of these adhesives is 11–12, due to the lime, sodium hydroxide, and sodium salts used for dispersion.

Casein can be dispersed with a number of alkalies at pH's of 7 and above, and with urea, an amide, at about pH 6. Isolated soy protein can be dispersed at a slightly higher pH. However, soy bean flour, the product used in the protein blend glues, requires a highly alkaline treatment in the pH range of 11–12. Animal blood can be dispersed in water to a certain degree, but for complete dispersion, alkaline treatment is also required. The use of the high pH alkalies has proven to be the successful route with this group of wood adhesives, because in addition to the dispersion factor, the lime provides water resistance.

### Chemistry of Protein Blend Glues

The key to formulating protein adhesives is understanding what happens to the protein under the influence of alkaline dispersion and in the presence of denaturing chemicals and conditions. Lambuth<sup>38</sup> discusses the complex chemical process. At a pH of 11–12 the protein molecules are almost completely and irreversibly uncoiled, freeing their reactive and polar groups for adhesive bonding. Hydrolysis into peptones, peptides, and amino acids further enhances the adhesive potential, but with loss of water resistance and bond strength, unless the formulator intervenes. Alkaline dispersion proceeds rapidly, hydrolysis more gradually. Thus, viscosity rises quickly from a low to a high plateau from which it will subside to a low value again over several hours. It is up to the formulator to build into the formula a few hours of relatively level viscosity. This is much easier with casein than with soy flour and blood, because the casein glues do not demonstrate a rise in viscosity as rapid as that shown by the other two protein sources. With proper formulation, it is possible to obtain several hours of fairly level viscosity with casein, before hydrolysis takes over, or before certain formulations carry the casein glue to a gel. Casein makes an excellent contribution to the water resistance. Addition of blood increases the water resistance even more, but soy flour causes a decrease.

Proteins are extremely prone to undergo a form of alteration described as *denaturation*. The elements which cause denaturation may be chemical or physical. The chemical agents of importance are: (1) the agents used for adding water resistance—lime, metal salts and oxides, formaldehyde and formaldehyde donors—and (2) organic chemicals such as alcohols and ketones which block the action of the crosslinkers by reducing the polarity of the solvent. The physical agent which is of importance is heat or any mechanical situation such as grinding or friction which develops heat.<sup>38</sup>

### Formulation and Chemistry of Casein-Lime Glues

The simplest formula for casein glue includes casein, light mineral oil, lime, and sodium

salts. The choice of sodium salts is restricted to salts of acids whose calcium salts are relatively insoluble. The sodium salts also cannot be hygroscopic and must not be capable of reacting with the casein, lime, or other chemicals in the dry state. The addition of oil retards the interaction of the casein particles with the chemicals until they can be completely wet out and also reduces the dustiness of the powdered casein glue. Upon addition of the dry glue powder to water, the lime (calcium hydroxide) and the sodium salts dissolve, yielding a highly basic solution. The sodium hydroxide, which is more reactive than the calcium hydroxide, disperses the casein, yielding essentially an ionized sodium caseinate. There is a slow reaction between the sodium caseinate and the excess lime, and the sodium caseinate slowly converts to the insoluble calcium caseinate. A simultaneous reaction is the hydrolysis of the casein molecule, a process which continues at an even slower rate.

The typical sodium salts include sodium fluoride, trisodium phosphate, soda ash, sodium bicarbonate, sodium sulfite, and others. The lime and sodium fluoride are essential for ready liquefaction of the glue. Casein may be dissolved with only lime, but this type of adhesive remains fluid only a short time before gelling. Additives, including defoamers and zinc compounds, and extenders, such as clays, wood flour, and shell flour, are frequently used.

The experienced formulator can customize a glue to perform specific jobs. At times a fast setting glue is important, but under other conditions, the glue must allow longer assembly time under warm conditions. The most successful formulas are closely guarded proprietary information. By finding the optimum balanced levels of sodium salts and lime, it is possible to control the viscosity of the wet glue in a manner which will provide a reasonable working life at a fairly level viscosity, and at the same time provide a glue with good dry and wet strength over the usable life of the wet mix.

The formulation of casein glues was described by Brown and Brouse.<sup>39</sup> Using 100 parts of casein as a constant, when the gram equivalents of lime and sodium salts are equal, the casein glue will have no water resistance. As the excess equivalents of lime over the so-

dium salts increases, the level of water resistance will increase. Formula 1 in Table 10 has water resistance, while Formula 2 has none.

It is the balance between the equivalents of sodium salts and lime that controls whether or not a glue gels. Within a given formula, when using the same glue powder-to-water ratio and the same casein content, incremental increases in sodium salts, lime, or both, can carry the glue from a gel to a nongelling glue. The viscosity of a gel glue increases rapidly, so most casein glues that gel have limited pot lives, an undesirable feature. Formerly some casein glue specifications required a gel glue to assure that the glue had water resistance, and to prevent use of the glue after hydrolysis set in. The gelling carried the glue through an unusable stage before the glue hydrolyzed.

In the earlier classification of casein glues by water resistance, a gel glue was the only example given for a glue which had water resistance. A glue which gelled only by the loss of water was described as non-water-resistant.<sup>40</sup> However, very water resistant casein glues which do not progress to a gel are available today. With these glues the excess lime is the primary key to the water resistance. Also, the mix ratio of water to dry powder influences whether the mixed glue demonstrates the gel tendency.

Some of the older literature speaks of a casein glue going through a very heavy stage before breaking down to a usable glue. Current formulations may be slightly heavier during the first 10 to 20 minutes after mixing with water, but the bodying up described for earlier formulations is not evident. This might be due to the better quality of the casein available today or to advances in formulating.

Casein from different countries of origin and even different lots from the same country can affect the viscosity pattern of casein glue. To maintain a predictable performance, minor formula adjustments must be made routinely.

These highly alkaline glues are not as susceptible to microbial attack as are the lower pH casein adhesives; however, addition of a fungal inhibitor is recommended for a glue to be used for a structural application. Salzberg warns that it should be clearly understood that fungal inhibitors protect only the glue line and the ad-

**Table 10. Formulas for Casein and Casein-Blend Glues (Dry Mix Type).**<sup>42,43</sup>

<i>Materials</i>	<i>Formula No. 1 Casein</i>	<i>Formula No. 2 Casein</i>	<i>Formula No. 3 Casein-Soy Blood</i>	<i>Formula No. 4 Casein-Soy</i>
Casein	59.1	70.8	36.0	15.0
Light mineral oil	3.6	3.6	2.6	3.0
Lime, hydrated	17.7	9.4	18.0	12.0
Sodium fluoride	2.5	2.8	2.5	3.0
Trisodium phosphate	11.2	9.0	7.6	—
Sodium carbonate	—	—	3.8	5.0
Sodium sulfite	3.7	4.4	—	—
Soluble Blood	—	—	2.0	—
Soy flour	—	—	24.0	57.0
Wood flour	1.0	—	—	5.0
Bentonite	1.2	—	3.5	—
Total Dry Parts by Weight	100.0	100.0	100.0	100.0
Water	165.0	200.0	200.0	250.0

jacent wood, not the bulk of the glued structure, which can support fungal growth unless separately protected. Because of leaching, a gradual loss of fungal protection may be expected when water soluble biocides are used.<sup>41</sup> *Sodium pentachlorophenate* is the fungicide with the longest history of successful use with casein glue, typically at 3% on the dry powder. In recent years only the glues that had to meet government specifications requiring a fungal inhibitor have been protected, because of increased concern about environmental impact of this type biocide in waste. Since recent Environmental Protection Agency (EPA) regulations, no biocide is being used in casein glue. See the Adhesive Specifications section of this chapter and Ref. 45. Use of other, safer fungicides is being investigated. In addition, other means, such as paint and epoxy coatings, plus protection from humid conditions, are being used to protect most casein-glued laminations from biological attack.

### Mixing Casein Glue

The formulas given in Table 10 are for the dry mix type of casein and protein blend glues which are currently in use in the United States. Several decades ago, the practice of formulating these glues as wet mixes was widespread, an approach which made a wider range of additives available. Frequently a phenolic resin

or sodium silicate solution was added, liquids which could not be incorporated into the dry mixes. Also, the components could be added in the most advantageous sequence. The dry mixes, however, had the strong advantage of convenience, and replaced the wet mixes over the years. Formulas for preparing wet mixes are given in the second edition of this Handbook, Chapter 10, Soybean Glues, and Chapter 11, Blood Glues.

The usual mix ratio for casein glue is 2 parts of water to one of dry glue powder; however, some casein-soy glues need a mix ratio as high as 2.5 : 1. Two kinds of mixers are used: a high speed double propeller type and a slower paddle type. With the preferred high speed type, the water is charged and the powder is added as fast as the mixer can introduce the material. With the low speed mixer, frequently a portion of the water is withheld, the lumps are rubbed out by agitation of the heavy mix, the remainder of the water is added, and the glue is mixed to uniformity. For both types of mixers, the glue is allowed to stand 10 to 15 minutes to allow time for the casein to dissolve, and is mixed again for several minutes before using. Casein glue develops an exothermic reaction when added to water, so the temperature of the water used should be about 5–6°C cooler than the desired temperature of the wet mix. Typically, 18°C water is used to give 24°C glue. Hot water should not be used.

### Additives for Casein and Protein Blend Glues

**Latex.** The bonds achieved with these glues may be improved with two classes of additives. Latex is used widely to improve the bonding of difficult-to-glue skins. The problems with these skins are manifold, usually caused by high density wood, by extractive heartwood, by resin which has been brought to the surface when the plywood has been manufactured in hot press, or by glazed surfaces caused by dull knives used to cut the veneer. Latex is frequently added to the casein-soy blend glues to improve the bond. It gives a plasticity to the glue line, a feature which reduces the brittleness of the cured casein or protein glue line, helping, as the lamination ages, to retain the normally high early (green) strength of the glue line.

The recommended latex for use with both casein and protein blend glues is a *carboxylated styrene-butadiene*, with a styrene content of 60 to 65%. When this latex has a pH of 7.5–8.5, it will increase the viscosity of the base glue and sometimes will require a higher dilution of water. When the latex has a pH of 9.0–9.6, the effect on viscosity will be minimal. The latex must be added to the mixed casein or protein blend glue, not to the water. The typical addition is one gallon of latex for one 50 lb bag of glue.

**Furfuryl Alcohol.** The use of furfuryl alcohol is recommended to counter the effect of certain acid-treated fire retardant woods and is covered by U.S.A. and Canadian patents.<sup>42</sup> This type additive extends the allowable assembly time by delaying the gelling action of the acid salts on the alkaline casein glue. The alcohol retards the reaction of the acid salts in the fire-retardant-treated lumber with the alkaline casein glue, and at the same time slows down the formation of calcium caseinate, which has a viscosity-building effect. Use of furfuryl alcohol reduces the ratio of water to dry powder needed to mix the casein glue. Furfuryl alcohol is recommended for use with casein glues or with casein-soy flour blend glues where soy flour is only a minor fraction of the protein. It is not recommended for the high soy content

glues. A level of 30% furfuryl alcohol, based on the dry casein glue, has been found to be effective, although lower levels will also extend the assembly time of the glue to a lesser degree. There is some use of diacetone alcohol for this purpose, but it is less effective than furfuryl alcohol. These additives are sold under the trade names assigned by the adhesive companies promoting them.

### Uses of Casein Glues

The casein wood glues have a long history of use as interior structural adhesives, assembly adhesives, and panel-to-frame adhesives. A limited but important use is as a nonconductive adhesive in the construction of spacers for the large transformer boards for the electrical industry. The most popular use of casein and protein blend glues is in the production of hollow and solid core flush doors, an operation for which these glues are ideally suited. Most of the doors in this country are made with this type of glue.

*Flush doors* are produced by bonding “skins” of plywood, hardboard, or particle board to the vertical and horizontal frames (the stiles and rails), which are usually either a soft wood such as fir or a man-made product comprising layers of pressed board. Hollow core doors utilize an accordion-type paper core, while a solid core door is constructed with a core of pieces of scrap wood edge-glued with an inexpensive casein-soy glue. Some of these cores are held to shape by corrugated cardboard, which is bonded to their surfaces with the same type of protein blend glue.

*Fire doors* are usually constructed by bonding plywood to a frame of fire-retardant-treated stiles and rails, made with either hard maple or a man-made hardboard, this frame having been fastened around a fire-resistant mineral core. Casein and casein-soy blend glues with and without the furfuryl alcohol additive are the primary adhesives currently selected for use in these operations.

### Specifications Applying to Casein Glue

The specifications most frequently used for casein glue are of two types: those specifically

written to apply to the generic adhesive, and industry specifications which control the end products for which casein glue is normally used.

**Adhesive Specifications.** There are two ASTM specifications covering casein glues:<sup>44</sup>

(1) ASTM D 3024-84, "Standard Specification for Protein-Base Adhesives for Structural Laminated Wood Products for Use Under Interior (Dry Use) Exposure Conditions." A request to drop this specification is currently in the balloting process. No conforming glue is currently being manufactured commercially for several reasons: a decreased demand for casein glue for structural purposes, availability of sodium pentachlorophenate only in the dusty powdered form (beads no longer available), and a recent EPA withdrawal of the registration of sodium pentachlorophenate for this application and others.<sup>45</sup>

(2) ASTM D 4689-87, "Standard Specification for Adhesive, Casein-Type"—This specification is a replacement for Federal Specification MMM-A-125-D, "Adhesive, Casein Type, Water and Mold Resistant."<sup>46</sup> Upon acceptance by the government, ASTM D 4689-87 will be the designated specification regulating the testing of casein glues for purchase by the Federal government, or for use by agencies filling government contracts. The new specification covers three categories: Class A, Water and Fungal Resistant; Class B, Water Resistant; and Class C, Dry Use (a new classification which will not require a test for water resistance). No conforming glue is currently being manufactured to meet Class A, but ASTM D 4300-88, "Standard Test Methods for Ability of Adhesive Films to Support or Resist the Growth of Fungi", may be used to test new biocides for compliance with the fungal resistance requirements. To meet the ASTM strength specifications, casein glue is tested with laboratory prepared birch plywood (ASTM D 906) and maple block (ASTM D 905) specimens.

**Industry Specifications.** The manufacture of doors in the United States is controlled by NWWDA Industry Standard, IS 1-86., written by the National Wood Window and Door As-

sociation. (A copy of Series 8, "Wood Doors," may be obtained from NWWDA, 205 W. Tough Ave., Park Ridge, IL 60068.) The glue lines of a finished door are tested for compliance with either: Type I, "Exterior Use," a two-cycle boil test, or Type II, "Interior Use," a three-cycle soak test. Casein glue is used to bond the skin (frequently plywood) and the frame, while other adhesives are used between the plies of the plywood, so if delamination occurs, it is important to pinpoint the location.

Casein glue easily passes the Type II specification. Casein-soy blend glues pass Type II if the percentage of soy flour is not too high. There are some highly water resistant casein glues that pass the Type I specification. Some of these glues are currently being used for exterior doors, although it is recognized that the doors must be painted or coated with a material which is impervious to water or humidity. It is important not to equate the NWWDA Type I bond with other much more highly water resistant Type 1 adhesives, such as the cross-linked polyvinyls, resorcinols and melamines.

**Canadian Specifications.** In Canada, CSA Standard for Wood Adhesives No. 0112.3-M 1977 covers the specifications for casein glue. Glue line requirements for wood doors are covered in CSA Standard 0132.2-M 1977. (Copies may be obtained from Canadian Standards Association, 178 Rexdale Blvd., Rexdale, Ontario, Canada, M9W 1R3.

### Viscosity and Pot Life

In addition to the bonding properties, casein glue manufacturers pay close attention to the viscosity and pot life of their products, when mixed using the recommended ratio of water to dry powder. A glue with a four hour pot life when tested under laboratory conditions will last approximately two hours in a plant situation, when subjected to the agitation of a spreader. Because the glues containing soy flour are more thixotropic, they are made in a slightly higher viscosity range; see Table 11.

### Certification of Fire Doors

Adhesives for use in making fire doors must be tested and certified within a licensed construc-

**Table 11. Viscosity Pattern of Casein and Casein-Soy Glues.<sup>47</sup>**

<i>Hours</i>	<i>Minutes<sup>b</sup></i>	<i>Viscosity, cp @ 25°C<sup>a</sup></i>	
		<i>Casein Glue</i>	<i>Casein-Soy Glue</i>
	20	4500	6500
1		3800	5000
2		3600	4800
3		4000	5500
4		6000	8000

<sup>a</sup>Tested with a Brookfield rotational viscometer.<sup>b</sup>Timed from the introduction of the glue powder to the water.

tion system, currently available from four companies: Weyerhaeuser, Georgia Pacific, Cal-Wood, and Masonite. The two certifying agencies for fire doors in the United States, Warnock Hersey (W-H) and Underwriter's Laboratories (U.L.), have lists of approved adhesives for each licensee's fire door construction, for 20, 45, 60, and 90 minute fire doors. The 20 minute fire doors are solid core doors, and do not require the special frames and mineral cores of the other fire doors; but they still require W-H or U.L. approval.

### Properties of Casein Glues

Casein glue is known as a very forgiving glue. It can be used under warm conditions at ambient temperatures as high as 100°F and under cold conditions, at temperatures in the range of 40°F. Because improved water resistance is related to a faster curing cycle, bonds developed at lower temperatures will show less water resistance than bonds developed at the optimum 60–80°F. It has also been demonstrated that with even warmer ambient temperatures, in the 90–100°F range, the water resistance will increase as the speed of cure is increased.<sup>56</sup> However, because of more rapid loss of moisture in the glue line under warm conditions, allowable assembly time is shorter. Casein glue works well with an assembly time which can vary from less than 10 minutes to over 30 minutes, a feature which is used to advantage in the door industry, where a stack of 40 to 50 doors is built before applying pressure. At temperatures of 65–80°F, sufficient strength will develop so that the stack may be removed from pressure after only 25 minutes, and may be trimmed only

a few hours later. Low temperature bonding requires a longer press time because of slower curing time.

Some of the earlier work of Browne and Brouse was reported in Ref. 1 by Salzberg.<sup>48</sup> Joints bonded with casein glue will average better than 90% wood failure when the following softer wood species are used: redwood, western red cedar, white fir, Sitka spruce, southern cypress, western hemlock, eastern red cedar, chestnut, red alder, and northern white pine. With the harder woods—red oak, maple, white ash, yellow birch, and persimmon—the joints will show 30–50% wood failure.

The highly alkaline casein-lime-sodium salt glues have a tendency to stain oak, maple, and some other species, a problem especially conspicuous in thin veneer. Discolored wood may be treated with sodium perborate and stained glue lines may be bleached with a dilute solution of oxalic acid. It is better, however, to avoid staining by preventing *bleed-through*. This may be accomplished by using drier stock, thicker glue, by releasing pressure sooner, and by drying the assembly immediately after pressing.<sup>50</sup>

### Durability of Casein Glues

In studies by Selbo and Johnson for Forest Products Laboratory, six types of joint designs, prepared with ten different adhesives, were subjected to three different humidity cycles over a period of three years. In maple wood joints bonded with casein glue containing preservative, the side grain-to-side grain joints retained the highest strength.<sup>51,52</sup>

Although the dried casein glue line is hard

and brittle, high frequency vibration of lap joints for 40 hours did not affect their strength. Glue lines 0.02 in. thick held up better than glue lines 0.002 in. thick, although initial shear strength was higher for the thinner glue lines.<sup>53</sup>

Casein glue has a history of use as an adhesive for interior structural laminated products, beams, trusses, girders, and columns. As evidence of the durability of the bond, there are structures laminated with casein glue which have been standing since the 1930s. The durability of the casein bond on wood increases when the preservative sodium pentachlorophenate is used to protect the glue line from the growth of fungi, a problem in the presence of conditions of heat and moisture. Selbo<sup>54</sup> found that Douglas fir beams far outlasted Southern pine beams, both bonded with casein glue without preservative, perhaps because of the lower moisture content of the fir at the time of gluing.

At the Department of Forestry in Canada, it was determined that when a lamination bonded with casein glue is stored at an equilibrium moisture content of 15% or less there is an equal rate of loss of the strength of the glue line and the wood substance. At higher moisture contents the glue line failed sooner than the wood. This study resulted in the requirement by the Canadian Specifications Administration that structural laminates bonded with casein glue shall not be used for installations where atmospheric conditions produce a wood moisture content of more than 15%.<sup>55</sup> Bergin<sup>56</sup> has shown that for a casein glue line in yellow birch, the dry strength is not affected by a wide variation in temperature, but the ultimate wet strength is higher as the storage temperature is increased.

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# Starch Based Adhesives

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Starch is a natural polymer, available in very large quantities and at relatively low and stable prices. It consists of glucose units chemically bound together so as to form a nonreducing polyhydroxy material. Because of the many hydroxyl groups, starch has a high affinity for polar substances such as water or cellulose. Starch can be reduced to low molecular weight sugars by enzymes called *amylases*, or by acid hydrolysis.

Some major changes in starch usage in adhesives and related fields are the large increase of cationic and amphoteric starches in paper manufacture and the increased use of high amylose starches in the corrugating industry.

The increased emphasis on recycling makes the use of starch desirable because amylases are able to degrade the starch with essentially no effect on the major part of the adherent matrix. There is a patent on the use of amylase as a release agent in starch glued materials recycling.<sup>1</sup>

Most of the starch used in adhesives in the United States is produced from corn or maize. There are four commercially available starch types that are used in adhesives. These are *waxy corn starch*, *regular corn starch*, *high amylose type V corn starch*, and *high amylose type VII corn starch*. The major difference between these starches is in the amount of amylose contained in them—approximately 0, 28, 55, and 70%, respectively, by iodine titration. Other starches usable in adhesives include sorghum

starch, potato starch, tapioca starch, wheat starch, rice starch, and sago starch. The term *sago* was originally applied to starch from the stem of *Metroxylon*-type palm trees, but is often used to describe starches from other palm trees, or even applied to some varieties of tapioca starch. Some characteristics of several commercially available starches are shown in Table 1.

Regular corn starch consists of two major fractions that can be separated by precipitation with butanol under appropriate conditions. The fraction that precipitates out is called *amylose*. Amylose is essentially linear in form, stains blue with iodine solutions, tends to form a rigid gel from concentrated solutions or to precipitate from dilute solutions, and is about 95% digested by beta amylase (a test for strict linearity or lack of branching) when very carefully isolated. Amylose forms strong, water-resistant films when a solution is evaporated.

The other main fraction is called *amylopectin*. Amylopectin is highly branched (one branch every 14 to 27 glucose units), stains brown to purplish with iodine solutions, tends to remain in solution at room temperature, and is digested to about 55% by beta amylase. Amylopectin forms weak, water sensitive films.

Regular corn starch (when carefully fractionated) contains an additional *intermediate fraction*. This fraction is precipitated out of the original corn starch solution by butanol, but is not reprecipitated when water and butanol are

**Table 1. Commercial starches. Approximate Data and Ranges.<sup>4</sup>**

Starch	Corn	Wheat	Rice	Tapioca	Potato	Sago
Source	Seed	Seed	Seed	Root	Root	Pith
Granule size in diameter microns	5–26	3–35	3–8	5–35	15–100	10–70
Gelatinization						
Temp. (°C)	62–72	58–64	68–78	49–70	59–68	60–67
Amylose (%)	28	25	19	20	25	26
Amylose (DP)	480	—	—	1050	850	—
Amylopectin (DP)	1450	—	—	1300	2000	—

added to the amylose fraction dissolved in dimethylsulfoxide. The intermediate fraction is precipitated by iodine from the various solutions, and is 5–7% of the starch in regular corn starch. The full analysis for regular corn starch is 25–27% fractionated amylose, 68% amylopectin, and 5–7% intermediate fraction.

When *waxy corn starch* is carefully fractionated, 2% intermediate fraction is found. The remainder is amylopectin.

*High amylose corn starches* differ from regular corn starch in that the high amylose corn starches contain more amylose, much more intermediate fraction and much less amylopectin than regular corn starch. For example, a high amylose type VII starch having 70% amylose by iodine titration contained 63% recrystallized butanol complex (standard amylose), 31% intermediate fraction, and only 5% amylopectin. About half of the intermediate fraction is probably low molecular weight amylose (19,000 daltons). This low molecular weight amylose fraction may be responsible for some of the rapid bond formation noted in corrugating adhesives using high amylose starches. The standard amylose determination (70%) is not fully indicative of possible performance. A better analysis would be: normal amylopectin 5%; low molecular weight, less branched amylopectin about 16%; low molecular weight amylose about 16%; high molecular weight amylose 63%. Total amylose is about 79%, and total amylopectin is about 21%.

Some of the true solution properties of starch appear to be related to the molecular weight of the amylose or amylopectin fractions. For example, the viscosity of jelly gums probably depends on the amylopectin molecular weight. The literature has tended to show increased

molecular weights as the methods of isolating the fractions of starch and the methods of determining molecular weight have improved. Most literature indicates that amylose has a molecular weight of about 1,000,000 to 2,000,000 depending on its source, and amylopectin has a molecular weight of about 400,000,000. These are weight average molecular weights determined by light scattering experiments of the fractions with the starch dissolved in dimethylsulfoxide. Commercially used starches probably have much lower molecular weights. For example, the amylopectin of one cultivar of potato starch was consistently determined to be 65,000,000, while the amylopectin from a second cultivar was just as consistently determined to be 440,000,000. A sample of waxy maize starch had a molecular weight of 400,000,000 but after shearing a 15% solution in boiling water the amylopectin molecular weight was determined to be 10,000,000.<sup>2</sup> At high molecular weights the error of measurement becomes quite large. The error at 100,000,000 is  $\pm 10\%$ , and at 500,000,000 the error is  $\pm 20\%$ . The amylopectin from pea starch appears to be the highest recorded, being 1,500,000,000 in one case.<sup>3</sup>

The terms *linear* and *branched* were used in the preceding discussion in describing amylose and amylopectin. Fig. 1 illustrates the way in which glucose units are linked together to form starch. Most of the glucose units in starch are linked in a (1-4)- $\alpha$ -D-linkage. All of the linkages are of this type in amylose (theoretically at least). This is called the *linear polymer*. Amylopectin contains, in addition to the above linkage, a (1-6)- $\alpha$ -D-linkage once in about 25 glucose units.<sup>4</sup> The 1-6 linkage is called a *branch point* and the linear extension

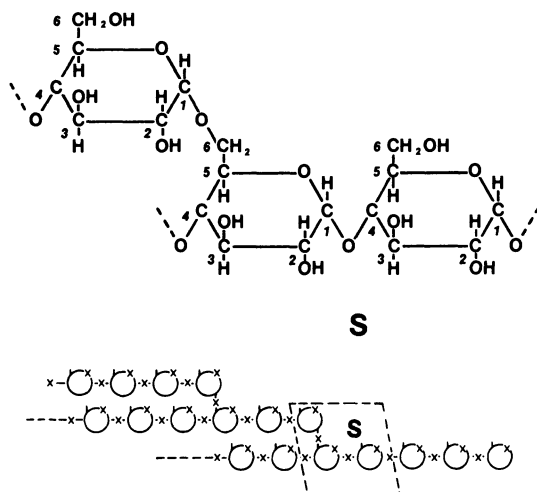


Fig. 1. Schematic representation of a segment of amylopectin molecule.<sup>4</sup>

of this branch point is called a *branch*. Amylopectin is therefore called a *branched polymer*. Many amylases are able to hydrolyze at both the 1-4 and the 1-6 linkages, but beta amylase hydrolyzes only at the 1-4 linkage. Further, beta amylase is able to attack only at the nonreducing end of the starch molecule, and hydrolyzes off one two-glucose unit at a time only if that unit is linked 1-4 (*maltose*). Hence, the low digestion by beta amylase (65% in some commercial amylose) suggests an occasional short branch in all except the most highly purified samples.<sup>5</sup>

When starch is suspended in water it tends to increase in volume and to absorb about its weight of water. If the temperature is slowly increased there is a point at which water absorption increases dramatically. The starch granule expands 10–100 times in volume depending on the type of starch. If the amount of starch present is greater than required to absorb all of the water available, then the viscosity of the starch dispersion becomes very heavy. The swollen granules can be partially destroyed by mechanical agitation, and the viscosity will decrease, depending on the type of starch. The temperature at which the starch suddenly swells when heated in water is called the *gelatinization temperature*.

The *unswollen starch* granule is in a crystalline state and as such is *anisotropic*. Most of the starch granules are *birefringent* under the

polarizing microscope, showing a “polarization cross.” These disappear at or near the gelatinization temperature when heated in water, indicating a loss of crystallinity. With further heating the granules tend to swell a little further, collapse to a degree, and fragment if sheared to any extent. Although some starches such as waxy starch, potato starch, tapioca starch, and sago starch cook to an almost clear suspension, the starch is not in solution. This can be seen by examining the starch cook with a phase contrast or interference contrast microscope, where the swollen granules or granule fragments are evident. Most starches start to swell at about 140–170°F (60–70°C), and appear to be reasonably dispersed at 203°F (95°C). In order to completely solubilize the starch a much higher temperature of 300–320°F (150–160°C) is required. Some granules in the high amylose starches tend to retain their polarization crosses above 212°F (100°C), but at the 300–320°F range these granules are also completely dissolved.

The cook texture of many starches can be explained by their composition. Waxy corn starch, which is all amylopectin, when heated at 8% starch solids in water becomes very heavy and cohesive as the granules swell. With continued heating, the viscosity decreases as the granules are broken up. On cooling, the viscosity increases. The texture remains cohesive, and the solution retains its clarity. This behavior is typical when the amylopectin fraction dominates the cook characteristics. Regular corn starch, at the same solids, is much thinner, behaves like a short paste, and is quite cloudy when hot. On cooling, the cook becomes an opaque, rigid gel. In this case the amylose has modified the hot cook characteristics of the amylopectin, and completely dominates the characteristics of the cooled cooked suspension. If the amylose has too high a molecular weight, then the gelling on cooling may not take place. Tapioca, potato, and sago starches behave more like waxy corn than corn, even though these are amylose containing starches.<sup>6</sup> These amylose containing starches will set to firm gels if the starch is degraded with acid (see *fluidity starches*). Many of the characteristics of common starches after cooking are given in Table 2.

**Table 2. Cook Characteristics of Native Starches (cooked 1 part in 15 parts water at neutral pH).<sup>4</sup>**

Starch	Hot Cook Body	Hot Cook Viscosity	Viscosity on Prolonged Cooking	Gel Formation on Cooling	Clarity (cold)
Corn	Short	Medium	Stable	Very high	Opaque
Wheat	Short	Relatively low	Stable	Very high	Opaque
Amioca	Stringy-cohesive	Moderately high	Thinning	None	Fairly clear
Tapioca	Stringy-cohesive	High	Thinning	Very low	Quite clear
Sago	Stringy-cohesive	Moderately high	Thinning	Moderate	Fairly clear
Potato	Gummy, very cohesive	Very high	Thinning	Very low	Very clear

Likewise, many of the adhesive properties can be explained by reference to the amylose and amylopectin properties of the starch used. *Jelly gums* are usually made from waxy starches (100% amylopectin) and are stable at room temperature for many months, as would be expected from the slow retrogradation rate of this starch. A corrugating formulation must set to form a bond and become water resistant in a short period of time. The low molecular weight portion of the amylose would be expected to come out of solution fairly rapidly to make a temporary bond, and the high molecular weight portion would more slowly tend to create water resistance.

## MODIFICATION OF STARCHES

The previous discussion was concerned almost exclusively with the use of native starches dispersed in water. The properties of the dispersions can be changed considerably by additives, or by modifying the starch. The principal modification in the adhesive industry is to decrease the molecular weight of the starch components so as to permit a higher solids content in the formulation. The starch is usually treated in granular form.

### Fluidity Starches

Fluidity starches are made by hydrolyzing the starch in *dilute acid* below the gelatinization temperature of the starch. The range of fluidities is 20–90, with a 90 fluidity starch being very much thinner than a 20 fluidity. Fig. 2 gives an indication of the concentrations required to produce a given hot viscosity.

### Oxidized Starches

A second modification to reduce viscosity is to treat the starch with *chlorine* under alkaline conditions. Lightly chlorinated starches use the water fluidity method of viscosity designation, but more heavily chlorinated products use a borax fluidity procedure. Chlorinated starches are generally called *oxidized starches*. They are *anionic*, in that they contain negative charges. This can be verified by staining with cationic dyes. *Methylene Blue* is a typical cationic dye.

### Dextrinization

A third method of reducing viscosity is by the use of *dry heat*, usually in the presence of

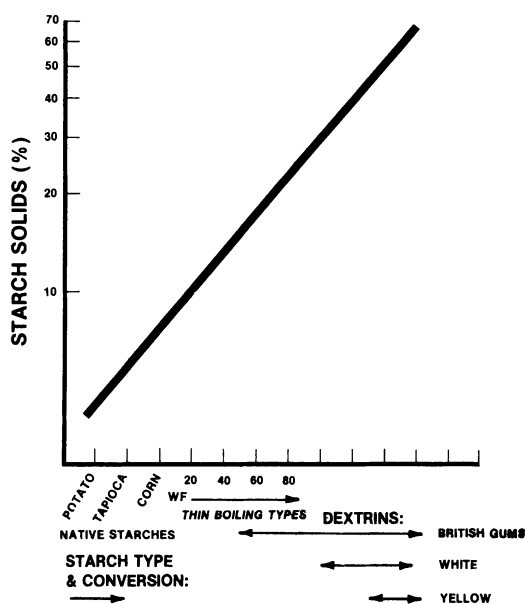


Fig. 2. Approximate concentrations of starch in thin flowing cooks (140°F).<sup>4</sup>

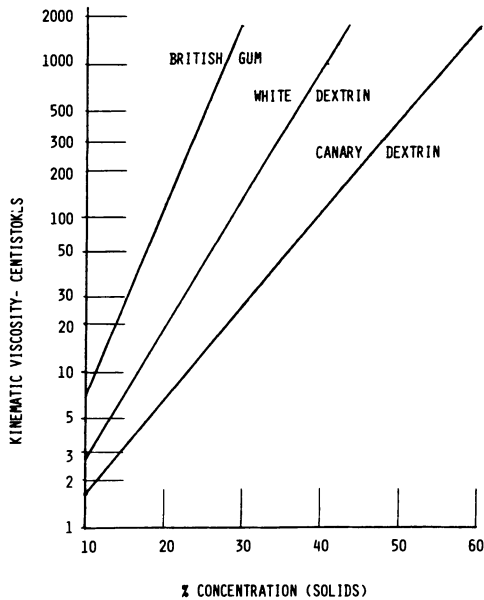


Fig. 3. Viscosity-concentration relationship of corn dextrans at 80°F.<sup>4</sup>

acids. This process produces *dextrins*. Their viscosity is also measured by using the *BF* or *borax fluidity* method. Dextrin viscosities are illustrated in Figs. 2, 3, 4. Other dextrin properties are given in Table 3.

### Hydroxyethylation

Starch is treated with *ethylene oxide* under alkaline conditions. The major purpose is to *slow down retrogradation*, or precipitation of amylose from solutions of starch. This is effective because the amylose tends to be uniformly substituted, whereas amylopectin is substituted mainly near branch points.<sup>7</sup>

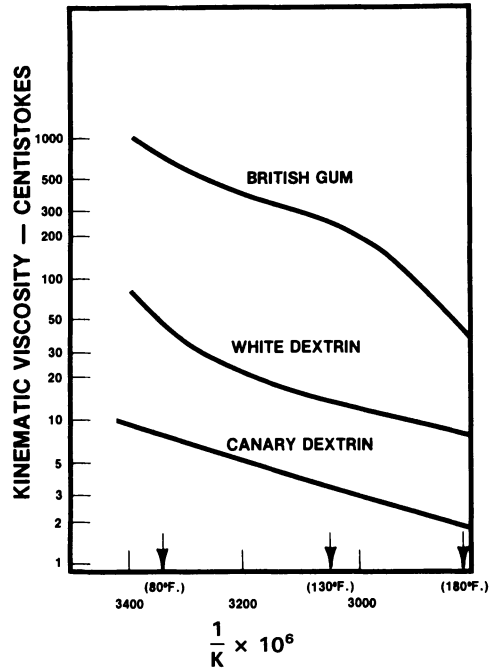


Fig. 4. Viscosity-temperature relationship of corn dextrans at 25% solids.<sup>4</sup>

### Cationic Starches

Starch is reacted with *tertiary* or *quaternary amine halides* or *epoxides* under alkaline conditions.<sup>8</sup> The cationic starches improve sheet strength, possibly through ionic bonding with slightly anionic paper. The cationic starches are also used in bottle-labeling adhesives and in paperboard.

### Amphoteric Starches

Cationic starches are phosphorylated by heating with *orthophosphate* to produce a starch with

Table 3. Comparison of Dextrans.<sup>4</sup>

Dry-roasting Process				Dextrin Properties			
Dextrin	Acidity	Moisture	Temperature	Degree of Polymerization (DPn)	Color	Cold water Swelling	Stability
White	High	High	Low	20	White	Partial	Limited
Yellow or canary	Low	Low	Moderately high	20-50	Light	High	Good
British gums	Very low - none	Very low	Moderately high to high	Very wide range	Yellow to dark brown	Partial to complete	Good

amphoteric (both cationic and anionic) properties. These starches offer improved pigment retention and dry strength over a wide pH range.<sup>8</sup>

### Miscellaneous Derivatives

These include *cross linked* or *inhibited* starches, *hydroxypropylated* starches, *phosphorylated* starches, starch *succinates*, *grafted* starches, and *carboxymethyl* starch.<sup>9</sup>

Most of the formulations using starch adhesives appear to be obtained by trial and error. The preceding listing of modifications and references is intended to enlarge the scope of possibilities for adhesive development. The discussion of the effects of amylose and amylopectin on starch dispersions serves a similar purpose.

## EFFECT OF ADDITIVES

### Sodium Hydroxide

Sodium hydroxide (also called caustic soda) will increase tack, tend to solubilize the starch to a greater degree, increase viscosity, increase cohesiveness, and also increase color. It is usually added after cooking in water, usually to the extent of about 0.5% based on total solids. The increase in pH tends to place negative charges on the starch, which tends to explain dispersion and higher viscosity.

### Borax

Borax (sodium tetraborate decahydrate) and sodium metaborate (essentially a mixture of borax and sodium hydroxide) change the properties of cooked starch dramatically. There is a large viscosity increase with increasing borax addition to about 15% (based on starch present); tack and cohesiveness are also increased greatly. Borax is used up to 10% based on starch and is usually added before cooking the starch. It acts by complexing with the starch to produce negative charges, and in addition tends to crosslink the starch. It is the *crosslinking* that causes the large increases in solution viscosity.

### Urea

Urea is a *plasticizer* that acts by forming solid solutions with starch and dextrans. The urea

tends to prevent crystallization of the starch or dextrin when a film is dried. It is used at 1–10% based on starch present. Other chemicals with similar effects are *sodium nitrate*, *dicyanamide*, *salicylic acid*, *thiocyanates*, *iodides*, *guanidinium salts*, and *formaldehyde*. (Formaldehyde can also crosslink under acid conditions or be used as a preservative).

### Glycerol

Glycerol acts as a *plasticizer* by slowing drying time, preventing excessive drying of a film. In this capacity it is a *humectant*. Other humectants are *ethylene glycol*, *invert sugars*, *d-glucose*, and *sorbitol*.

### Soluble Soaps

These are used as *lubricants* to impart flexibility regardless of atmospheric conditions. Too much lubricant will weaken adhesive bonds. Other lubricants are *sulfonated castor oil* and *sulfated alcohols*.

### Urea-Formaldehyde Resin

This resin is added to give *water resistance*. *Resorcinol-formaldehyde*, *poly(vinyl acetate)*, *acrylics*, and *poly(vinyl alcohol)* are also used to increase water resistance.

### Miscellaneous Additives

*Clays* and *bentonites* are used as *fillers* in adhesives. *Sodium bisulfite*, *hydrogen peroxide*, *sodium perborate* serve as *bleaches*. *Solvents* are added to help wet water-repellent surfaces. *Preservatives* prevent microbial growth. *Defoamers* prevent foam during cooking. *Colloid stabilizers* such as *soaps* and *sodium chloride* are often added.<sup>10,11</sup>

## STARCH ADHESIVES

To be useful as an adhesive, starch must be dispersed in water, usually hot water, and a number of chemicals are added to modify the properties of the starch dispersion. The dispersion and formulation can be done by the user from the different types of starches or modifications of starches previously described. Or the user may purchase formulated adhesives from adhesives manufacturers.

### Jelly Gums

These are used for *bottle labeling*. They are prepared by treating waxy starch or waxy fluidity starch with caustic under high shear. The starch swells in the caustic, and most of the caustic is neutralized with nitric acid. One formulation yields a final composition of 39% starch (40 fluidity waxy), 3% urea (an additive), 3% sodium nitrate (from the sodium hydroxide and nitric acid used), and 56% water (Ref. 10, p. 605). The viscosity as used is about 100,000 cP. The labels are cold water resistant.

### Other Liquid Formulations

Alkaline starch formulations (prepared by adding enough caustic to gelatinize the starch) are used as carriers in *corrugating*, in *foil-to-paper* adhesives, and in *carton or case sealing* adhesives. If the caustic used to gelatinize the starch is neutralized, the adhesives at 18–25% starch solids are usable for *wall paper printing* or *foil-to-paper lamination*. Combinations of starches and water with added salts are the simplest adhesives, and can be used in *bill posting*, *bag making*, and *tobacco seam gluing*.

### Pastes

Short, soft, nonstringy adhesives formulated from heavy bodied starches or dextrins are called *pastes*. A typical formulation for *library paste* is to cook a mixture of 45% low-soluble white dextrin, 5% corn starch, 5% glycerol, and 45% water.<sup>4,10</sup>

### Borated Dextrins

Dextrins are frequently formulated with borax, sodium metaborate, boric acid, or caustic in different proportions to give good tack and higher stable viscosities at moderate concentrations. The pH of the formulations is about 9.0 in most cases. Borated dextrins find use in case sealing, carton sealing, tube winding, and laminating.

### White Dextrins

White dextrins are prepared by heating dry starch containing relatively large amounts of acid at low temperatures (258°F, 120°C) for rather short times (3–7 hours). Their color is

white to cream, and their solubility and viscosity varies from low to high. They are used in *bag-seam*, *tube winding*, *case and carton sealing*, *laminating*, *gummed sheets*, *label*, and *envelope back seam* adhesives.

### Canary Dextrins

Canary dextrins are prepared by heating dry starch containing a moderate amount of acid at moderate temperatures (300°F, 149°C) for a moderate time (11 hours). They are very light to dark tan in color, have a high cold water solubility, a low stable viscosity, and excellent re-moistening ability. They are used in *gummed tape*, *envelope front seals*, *stamps*, *case and carton sealing*, *laminating* and *tube winding*.

### British Gums

British gums are prepared by heating dry starch with a low amount of acid at high temperature (330°F, 166°C) for a long time (17 hours). They have low to high solubilities and low to high stable viscosities, dark color, and fast tack. They are used in *solid fiber laminating*, *bag-seam pastes*, and *tube winding* adhesive.

### Waxy Starch Dextrins

Waxy starch dextrins are similar to dextrins made from non-waxy starch, but have a greater viscosity stability than the corresponding regular dextrin. *Envelope front seals*, *stamps*, and *gummed sheets* are some uses.

### Dextrin/Silicate Blends

*Fast tack*, rigid films, low viscosity, and very good adhesion are obtained from this combination. *High speed case sealing* and *fiber foil cans* are some uses.

### Pregelatinized Starches

Pregelatinized starches are prepared by heat swelling a starch-water slurry, drying, and grinding the dry powder. The starch at 40% solids is fed to a steam-heated drum where it is gelatinized and dried, and finally scraped off the drum with a blade. These starches are used in some one-tank *corrugating* applications, *multiwall paper bags*, *wallpaper*, and *bill posting*.



## APPLICATION AREAS

### Papermaking

*Cationic*, *anionic*, and *amphoteric* starch derivatives are cooked and added at the wet end of the papermaking machine at 5–20 pounds per ton of paper. The starch flocculates pigments and fine pulp particles, improves retention of fines, helps drainage, and increases internal (Scott bond) and burst (Mullen) strengths. The starches are retained by the pulp because the pulp has a slight negative charge, which holds the positively charged starch. The positive charge is present directly in the cationic and amphoteric starches, and is formed by complexing with alum in the case of anionic starches.

*Unmodified starch* is also used at 20–40 pounds per ton of pulp. It is retained mainly by entrapment.

Although starch is largely added at the wet end of the paper machine, it can be placed directly on the formed sheet. The starch can be sprayed onto the fibers, applied as foam directly on the wet web, or applied as a thin curtain to the wet web.<sup>12</sup> These alternative methods have certain advantages, but they lose the flocculating ability of cationic or amphoteric starches.

### Paper Coating

In addition to adding starch at the wet end to hold the fibers together, starch can be added at the *size press*, at the size press with a pigment, at the *calender stack*, or as a pigmented coating as a separate operation. In all of the above applications, starch acts to bind the paper fibers together or to bind the pigment particles together or to bind the pigment to the fiber. The paper has been partially dried at the size press. The viscosity of the starch solution must be relatively low (50 cP) at the size press. The 2–12% solids used in coatings would have too high a viscosity. Therefore a viscosity reduction is usually necessary. This can be accomplished by enzymes or heat treatment in the case of regular starches, or oxidized, hydroxyethylated, acid fluidity, or acetylated acid fluidity starches can be used.

Oxidized starches are anionic, and if recy-

clered may cause pigment and fines retention problems in the wet end. *Cationic starch* which has been preconverted to a low viscosity appears to have advantages in physical properties of the paper and in retention of the surface sized broke.

Starch is added at the calender stack for curl control, surface strength, laying of surface fuzz, clay coating holdout, printing characteristics, and grease or oil resistance. Solids vary from 2 to 24%, depending on the starch type used and on the paper requirements. Low viscosity starches, hydroxyethylated converted starches, and oxidized starches are used in this application.

Similar starches to those used on the size press can be used in *pigment binding* applications, but the viscosity of the starch should be lower. A possible formulation for a 59% solids coating is 0.2% sodium hexametaphosphate, 10.1% calcium carbonate, 40.5% clay, 8.1% low viscosity starch, 0.05% pine oil, and 0.21% soap.<sup>4</sup> Thin boiling cationic starch has also been recommended for this application.<sup>12</sup> The same starches as are used above can be used when starch is added with pigment at the size press. Solids are generally 30–40%, and the starch to pigment ratio can be as high as 1 to 1. The viscosity is usually below 300 cP.

### Corrugating

Most of the corrugated board is made using the *Stein Hall* system, which consists of a mixture of *gelatinized starch* (called the *carrier starch*) and *ungelatinized starch*. Flat corrugating medium is fluted, starch is applied to the fluted tips, and a heated liner is brought in contact with the fluted tips under heat and pressure to produce a single facer. Adhesive is applied to the fluted tips on the other side of the corrugating medium and a flat liner called a *double backer liner* is applied. When the facers are brought in contact with the flutes containing the adhesive, the ungelatinized starch gelatinizes. This creates an extremely high viscosity at the flute-liner interface. The applied heat also evaporates water and further increases the flute-liner bond, so that the corrugated board can be cut without delaminating. The formulation includes *sodium hydroxide* and *borax* to decrease

the gelatinization temperature of the raw starch and to increase viscosity at the flute after gelatinization.

A typical old formulation is: put 13 parts water, 3.2 parts starch, 0.54 parts caustic dissolved in 0.8 parts water into a tank (called tank 1, or the upper tank), heat with steam to 160°F, agitate 15 minutes, and then add 16 parts cold water. This gelatinizes the starch present and makes the carrier starch portion of the adhesive. In another tank (called tank 2, or the lower tank) 49 parts cold water is mixed with 0.54 parts borax and 18 parts starch is added. The contents of tank 1 are slowly added to tank 2 with efficient mixing.<sup>4</sup> It is possible to carry the entire operation out in tank 2, but control is more difficult.

So called *no-carrier* or single-component systems depend on careful control to gelatinize the correct proportion of the granules present. One formulation, which increases water resistance by adding urea-formaldehyde, is: mix 20 parts starch, 77 parts water, 0.8 parts 50% caustic, and stir at 101°F until the viscosity reaches 25 Stein Hall seconds. Then add 0.04 parts alum, 0.4 parts boric acid, and 3 parts 60% urea-formaldehyde resin.<sup>4</sup> Other ways to make "no-carrier" systems are to add exactly the correct amount of caustic and stop the swelling by addition of boric acid; control the swelling by carefully injecting steam into the mixture; or partially swell the granules by milling a 10–40% moisture starch to damage granules before suspending in water.<sup>12</sup> A chemical-mechanical method of producing the carrier starch is to introduce a mixture of 12% starch and 30% caustic into a centrifugal pump. Final alkalinity was 14.4% and the viscosity was 4200 cP. at 76°F.<sup>13</sup> The use of starches having different gelatinization temperatures is given in Ref. 14. Here 350 parts tapioca starch and 3000 parts corn starch are suspended in 9000 parts water and treated with 500 parts 20% caustic at 38°C. (100°F). Then 55 parts of borax are added. The Stein Hall viscosity is 52 seconds, and the gel point is 63°C (145°F). The tapioca starch swells before the corn starch, and essentially produces the two-component system.

High amylose starches improve water resistance and increase speed of corrugation. A formula for the carrier starch is: 1192 parts water,

424 parts high amylose starch, 6 parts borax; bring to 130°F (54°C) and add with stirring a mixture of 36.6 parts caustic in 47.5 parts water. The raw starch portion is made by mixing 3480 parts water, 1600 parts corn starch, 28 parts borax and 91.2 parts thermosetting resin. Mix the carrier into the raw starch.<sup>15</sup>

It appears, at least in the case of high amylose carrier starch, that the carrier starch is the principal adhesive.<sup>16</sup> The raw starch, when gelatinized, absorbs water to concentrate the dispersed high amylose starch on the flutes. Older ideas of the mechanism were that the carrier starch was simply a suspending agent for the raw starch, which was the principal adhesive. One suggestion was that amylose migrating out of the granules caused at least the initial tack.<sup>12</sup>

There are many publications on the use of high amylose starches. High amylose starch is esterified with *acetic anhydride* or *succinic anhydride* to improve stability.<sup>17</sup> Another patent concerns the addition of *dihydroxyethyleneurea* together with *acetone-formaldehyde* to improve water resistance.<sup>18</sup>

The use of high amylose starches in the production of *cold corrugating* adhesives (not requiring extensive heating) has been published. A mixture of oxidized and hydrolyzed 70% amylose containing starches is dispersed as a 35% starch suspension, gelatinized at 140°C, and used in corrugating without steam. The high amylose starch was treated with 4% sodium hypochlorite at an initial pH 11 to make part A of the degraded mixture. Part B was made by hydrolyzing high amylose starch for 12 hours at 50°C (122°F) with 6% of 35% hydrochloric acid. Both A and B were neutralized to pH 5, washed, filtered, and dried. Then 70% A and 30% B were mixed to a 35% suspension and cooked at 140°C. The use of the B portion is claimed to improve speed from 90 m/min to 230 m/min.<sup>19</sup>

Mixtures of waxy, regular, and high amylose starches are degraded with a mixture of sodium persulfate, sodium sulfite, boric acid, and caustic, and cooked at 90°C (194°F) and about 33% solids to form a starch adhesive that hardens on cooling.<sup>28</sup> The cold corrugating process is described in other references.<sup>26–28</sup>

Other claims for improving corrugating formulations include increasing the carrier starch

solids,<sup>21</sup> addition of urea,<sup>22</sup> using crosslinked starch in the carrier,<sup>23</sup> and using cationic starch as the carrier starch.<sup>24,25</sup>

### Bag Adhesives

Three adhesives are used in paper bag manufacture: side seam adhesives, bottom paste adhesives, and cross pastes. The *side seam adhesive* is used to form a cylinder from a flat sheet of paper. This adhesive must develop a strong bond quickly, so the tube can be cut for further operation. The viscosity should be about 3,000 cP. and solids about 25%. One formulation is: water 68%, dextrin 28%; heat to 160°F (71°C), add 3% borax, heat to 190°F (88°C), add 3% preservative.<sup>4</sup> A *water-resistant* formulation is: water 1700 pounds, white dextrin 700, soap 2, urea-formaldehyde 70, heat to 200°F (93°C), dilute with cold water to 260 gal volume, and add 14 pounds ammonium chloride. This formulation should be used immediately. Its pH is about 6.<sup>4</sup>

*Bottom paste adhesives* are applied to one end of the tube formed above to close that end to form a bag bottom. These pastes are usually made from unconverted starches. Soap and/or salt may be added to produce a *thixotropic* paste (flows under shear but sets up if left undisturbed).<sup>11</sup> A *water-resistant* formulation is corn starch 13%, poly(vinylalcohol) 4.5%, poly(vinylacetate) 1%, soap 0.1%, water 81%, heat to 90°C (194°F), cool to room temperature.<sup>10</sup>

*Cross paste* is used for multiwall bags to glue the plies together before forming a tube. This is similar to seam paste, but should not penetrate the ply. Clay or poly(vinylacetate) is added to prevent penetration.<sup>10,11</sup> The *seam adhesive* for multiwall bags can be somewhat heavier than given above, and higher molecular weight white dextrans can be employed. The *bottom adhesive* is usually a fluidity starch.<sup>11</sup> A mechanical way of converting potato starch for use in paper bags is also described.<sup>29</sup>

### Laminating Adhesives

The requirements of the particular equipment must be met for bonding paper to paper or to paperboard, for making poster displays, bond-

ing paperboard to paperboard, or rotary lamination. *Lay-flat*, or *noncurling*, is an important attribute of these adhesives. High tack and low penetration are also required. One formulation is water 43%, high soluble white dextrin 21%, corn starch 4%, sodium nitrate 32%; heat to 200°F (93°C), hold 20 minutes, add preservative.<sup>4</sup> Another formulation is high soluble white dextrin 20%, clay 13.5%, urea 6.7%, borax 5%, water 55%.<sup>10</sup>

*Foil laminations* usually call for resins, but even here a small amount of starch is often added for its smoothing properties. One example is: poly(vinylalcohol) 3, starch 3, water 49, potassium persulfate 0.1; add dropwise a mixture of 5 dibutyl phthalate and 39 vinyl acetate at 70°C (158°F), dilute to 25% solids.<sup>30</sup> Starch at 3–15% is claimed to prevent coarse particle formation in the following formulation: 45% aqueous emulsion containing 1:99 acrylic acid: vinyl acetate copolymer 100, corn starch 4, poly(vinylalcohol) 5, dibutyl phthalate 15. Aluminum foil was coated on paper at 300 m/min (meters per minute) without coarse particle formation, while a similar formulation omitting the starch formed coarse particles at 90 m/min.<sup>31</sup>

### Tube Winding

Tube winding is either *spiral* (a continuous winding where adhesive is applied to outer plies as they are wrapped on a cylindrical mandrel), or *convolute* (where the sheet is as wide as the mandrel is long, and the mandrel wraps the sheet over itself). The tube is removed from the mandrel by a pusher arm. Convoluted adhesives are usually used cold, while spiral adhesives may be used at 131°F (55°C). Many starch products may be used, but 50% solids borated dextrans are common, as seen in Table 4.

### Corrugated Boxes

The tops and bottoms of corrugated boxes are closed with *case sealing adhesive*. Although liquid glues and hot melts are preferred, carton adhesives are used, sometimes with added caustic. Carton sealing involves bonding the bottom and top flaps of folded paper boxes. A

**Table 4. Adhesives in Packaging Applications.<sup>4</sup>**

Use, Function Type of Adhesive	Major Requirements	Acceptable Adhesives Base	Approximate Solids (%)	Viscosity Requirement (cps) (Brookfield Spindle/RPM/°F)
<b>Bag Adhesives:</b>				
Cross pasting	Tacky and quick setting	Starch-dextrin- mineral filler	25–30	—
Seam adhesives	Well machining slower	Starch or borated dextrin	5–39	2800 (RV 4/20/80)
Bag bottom pastes	Heavy, short	Raw starches or converted borax	15–30	—
<b>Laminating:</b>				
Mounting	Rapid tack, good open time, nonwarp	Dextrin and low viscosity starches	50	3800 (RV 4/20/75)
Rotary laminating	High tack	White dextrin with urea or sodium nitrate	55	4000 (VR 4/20/80)
Foil laminating	Adhesion to foil	Alkaline glues resins (PVAC) <sup>a</sup>	60	2700 (RV 4/20/75)
Tube winding	Tough, fast bond	Borated dextrin	48	2500 (RV 4/20/80)
<b>Corrugated Box:</b>				
Manufacturer's joint adhesive	Rapid tack, good open time	PVAC <sup>a</sup> , Hot-melt PVOH <sup>b</sup>	60	2000 (RV 4/20/75)
Built-up pad adhesives	Nonwarp	Dextrin borated dextrin	35–36	1000 (RV 3/20/75)
Case seal adhesive	Very fast, nonwarp	Canary dextrin borated white dextrin resin	40–50	—
Tray maker adhesive	Rapid setting	PVAC <sup>a</sup> Hot-melt	59	800/1000 (RV 4/20/80)
<b>Set-up Box:</b>				
Machine laminating	Quick setting, nonwarping	Animal glue and sugar, canary dextrin	70	
Hand laminating	Lay flat	Borated, white dextrin	48	
Ender pastes	Good flow and tack	Borated dextrin	50	400 (RV 3/20/80)
<b>Label Adhesives:</b>				
Porous substrate adhesives	Thin white	Borated dextrin	30	350 (RV 4/70/80)
Plastic container	Adhesion and high tack	PVAC <sup>a</sup> (Highly modified starch)	52	4000 (RV 4/20/80)
Can labeling	Tack and adhesion	Converted starch	33	4000 (RV 6/20/72)
Glass bottle	High tack	Jelly gums dextrin	40–50	
Notes: <sup>a</sup> PVAC = polyvinylacetate <sup>b</sup> PVOH = polyvinyl alcohol				

top and bottom carton sealing adhesive is water 51%, white dextrin 37%, preservative 1%, borax 6%, antifoam 0.06%; cook to 185°F (85°C) for 20 minutes, cool to 120°F (49°C), add 5 water and 0.6 of 50% caustic.<sup>4</sup>

### Gummed Tapes

The types of remoistenable tapes are regular sealing tapes, reinforced sealing tapes, and box tapes. A regular sealing tape formulation is: thin boiling waxy starch 44, urea 6, water 50.<sup>10</sup> For reinforced tape, thin boiling waxy starch 39.5, canary dextrin 17, polyacrylamide 2, dispersing agent 0.4, water 41.1 is suggested.<sup>10</sup> *Box tape* is usually made from animal glue, but one patent claims performance superior to animal glue from a starch acrylamide graft copolymer prepared as follows: water 51%, sodium nitrate 7%, waxy corn starch 33%, copper sulfate 0.03%, acrylamide 10%; mix, then add 0.05% ammonium persulfate and 0.03% sodium metabisulfate; heat rapidly to 200°F (93°C) and maintain for 15 minutes. Add sodium tartrate to adjust pH to 5.5.<sup>32</sup>

The use of an oxidized starch acetate 180, urea 20, and water 200 as a gummed tape adhesive has been patented.<sup>33</sup> The formulation of an acrylamide starch graft polymer is also claimed: hydrolyzed low viscosity acrylamide-starch graft copolymer 67, canary dextrin 20, animal glue 10, urea 10, petrolatum 0.25, and sodium hexametaphosphate 0.1, are heated for 30 minutes at 185–205°F (85–96°C).<sup>34</sup>

### Label and Envelope Adhesives

The general adhesives for these uses can be found in Table 4. Dextrins, enzyme-converted starches, or mechanically degraded starches are suitable, with white or canary dextrins made from tapioca, waxy corn, and regular corn starches the most used. The *envelope front seam* is *remoistenable* and can have 55–65% solids with a viscosity of 2,000–10,000 cP. After drying the adhesive should be non-blocking at high humidity. This requires a *nonhygroscopic plasticizer*. One formulation containing poly(ethylene glycol) is high soluble waxy corn dextrin 63, sodium bisulfite 1, Carbowax 4,000 (Union Carbide) 0.5, water 35.5.<sup>10</sup> Backseam adhesives can be a little thin-

ner with viscosities close to 1000 cP, and 40–50% solids.

*Discrete particle, flat gumming*, solvent-based adhesives are another method of making remoistenable adhesives. The cold-water-soluble material (usually a dextrin) is suspended in a solvent and applied to the paper and dried. Since the dextrin is not soluble in the solvent, it is deposited in discrete particles. On contact with water, the dextrin swells and will glue two pieces of paper together. The dextrin is usually used at 40% solids and a viscosity of 1000 cP.<sup>4,10</sup>

### Paper Box

Paper box manufacture involves the operations of *ending* (box body formation), *stripping* (coating the box walls with precut wrap and smoothing), *tight wrap* (machine wrapping a box with glue on most of the wrap), and *loose wrapping* (adhesive only on border of the wrap). Borated dextrins containing 10–15% borax and cooked at 30–50% solids are usually used. See Table 4 for more information.

### Textiles

Starch is used predominantly in *warp sizing* in the textile field. The purpose is to strengthen the yarns for weaving operations. A typical formulation is corn starch 8.5%, softener (tallow or sulfonated oil) 1.5%, kerosene 0.2%, cook to 190°F (88°C), and homogenize at 2000 psi.<sup>4</sup> Oxidized starches are used in finishing and printing, and low treatment starch acetates, starch monophosphate blended with poly(vinyl alcohol), cationic and amphoteric starches, as well as fluidity starches are used in finishing and warp sizing.<sup>35,36</sup>

### Wall Covering Adhesives

These require good wet tack and good slip. Plasticizers give slip (the ability to move the paper around to obtain a good fit), borax gives tack, and clay allows easier removal of the paper later. A formulation consists of acid modified pregelled starch 25, clay 20, urea 3.75, sodium metaborate 1.25, and water 50.<sup>10</sup> A remoistenable composition containing other polymers is: dry blend carboxymethyl cellulose

25, hydroxyethyl cellulose 8.5, sodium alginate 0.5, anionic polyacrylamide 0.3, urea 30, potato starch 27, colloidal silica 1, sodium stearate 2.5, sodium soap 3.5, sodium fluoride 0.5, and 4-chloro-meta-cresol 1. The mixture is suspended in 3 parts water, coated on paper and dried.<sup>37</sup> A second formulation is: starch 375, carboxymethyl cellulose 400, urea 200, polyacrylamide 5, colloidal silica 5, para-chloro-meta-cresol 10, sodium fluoride 5.<sup>38</sup> An *inverted emulsion* formulation containing a starch graft copolymer has also been suggested for wallpaper adhesives.<sup>39</sup>

### Miscellaneous Uses

Gelatinized starch 100, dextrin 100 is used to make fish food stable in water.<sup>40</sup> A 1:1 mixture of starch and polyacrylamide was used to make an adhesive for *high voltage transformers*.<sup>41</sup> A mixture of poly(vinyl acetate) emulsion 100, plasticizer 20, and starch 20 has been used in *book binding*.<sup>42</sup>

### GOVERNMENTAL REGULATIONS: ADDITIVES

The Food and Drug Administration (FDA) of the U.S. Department of Health, Education and Welfare (HEW) has issued a series of regulations concerning the use of potentially toxic substances in packaging materials contacting food. Most of the regulations may be found in the Code of Federal Regulations, Title 21, revised annually (21 CFR 121.2520, "Adhesives").

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# Natural Rubber Adhesives

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## INTRODUCTION

This chapter reflects the changes in the technology of one of the natural materials which was used as an adhesive long before modern synthetic polymers and which still maintains an important place. The chapter includes a few formulations from the first edition of this Handbook,<sup>1</sup> others have been revised. More importantly, over the second and the present editions the introduction of natural rubber grafted with methyl methacrylate has been accompanied by greatly improved grading systems for the more simple product as well as chemically stabilized and chemically depolymerized products. Reclaimed rubber must now be regarded as obsolescent in the adhesives industries of advanced countries, partly because of its uncertain composition but partly on economic grounds; it may still have a place in autarchic economies.

## RAW MATERIALS

### Natural Rubber Latex

Latex is tapped from the tree *Hevea brasiliensis* and contains about 35% solids. It is immediately ammoniated to prevent bacterial attack and coagulation. The field latex from the indi-

vidual trees is transferred to collecting tanks, and from this stage its treatment is determined by its destination. If it is to be marketed as latex, it is converted to concentrate; otherwise it is coagulated, sheeted or crumbed, dried, and baled for use as dry rubber. Natural rubber latex grades are described by the method of concentration and the type of preservative system used. Three methods of concentration are used: evaporation, creaming, and centrifuging, and a combination may be used in some special grades.

*Evaporated latex* is produced by heating at a reduced pressure, the ammonia usually being replaced by potassium hydroxide with the addition of a small amount of soap to assist stabilization. It has a solids content of about 73%. Also available is an ammonia preserved grade with 62% solids content. Retention of the proteinaceous and other non-rubber components during concentration results in greater colloidal stability than other types exhibit, and improved resistance to aging, but discoloration and moisture absorption are greater. The stability of evaporated latex is useful in some applications involving addition of a high level of filler.

*Creamed latex* is prepared by adding fatty acid soap and a creaming agent such as an alginate, after which it is stored in large tanks



until separation of the creamed layer from the serum is complete. Total solids content is 66–69%. Preservation is by ammonia, normally 0.70–0.76% wt/wt, although low ammonia latex is available with secondary preservatives. Creamed latex has no special properties of interest to adhesives manufacturers and is not normally used by them.

*Centrifuged latex* is by far the most important type, accounting for about 95% of latex production. A significant proportion of the water soluble non-rubber components is removed by centrifuging or creaming. It is usually safe to assume that natural rubber latex formulations will be based on centrifuged latex unless otherwise specified.

*Double centrifuged latex* is made by diluting centrifuged latex and recentrifuging. As a result of this, the non-rubber content (TSC – DRC: total solids content minus dry rubber content) is reduced significantly. This is of interest mainly in medical applications.

*Sub-stage centrifuged latex* is produced by creaming to about 50% solids content and then centrifuging. This enables a higher solids (67%) to be achieved.

*CV latex* is a grade which is treated at an early stage with a small amount of hydroxylamine to inhibit storage hardening.

## Preservation

A number of preservative systems are in use (Table 1). Evaporated latex may be preserved by ammonia or potassium hydroxide. Centrifuged latex is always preserved by ammonia, either on its own as in high ammonia (HA) latex or at a lower level in combination with a secondary preservative as in grades of low ammonia (LA) latex. The LA grades are typified by the type of secondary preservative, of which

the most important grade commercially is LA-TZ latex. Natural rubber latex is sold to specification, ISO 2004:1979 for creamed and centrifuged latex and ISO 2027:1978 for evaporated latex.

## Dry Natural Rubber

Eight basic natural rubber types are recognized internationally by appearance and description only. These are:

1. Ribbed smoked sheets
2. Pale crepes
3. Estate brown crepes
4. Compo crepes
5. Thin brown crepes (remills)
6. Thick brown crepes (ambers)
7. Flat bark crepes
8. Pure smoked blanket crepes

The definition of these grades is described in the so-called Green Book<sup>2</sup> and summarized elsewhere.<sup>3</sup> Only the first two grades are produced by deliberate coagulation of field latex, although grade 8 is prepared by reworking smoked sheet. The other types are derived from various adventitious forms of scrap which have been subjected to a cleaning process. In this system, the rubbers normally used for preparing adhesive solutions are type 1 (e.g., RSS1) or type 2 grades (pale crepe).

In 1965 a system based upon technical specification was introduced under the description Standard Malaysian Rubber (SMR). This is sold in the form of crumb compressed into 33 $\frac{1}{3}$  kg bales wrapped in polythene. The bale carries a standard mark which identifies source, weight, grade and also the viscosity number if it is a viscosity-stabilized rubber. This is illustrated in Fig. 1. Similar schemes are operated by some other producing countries. The SMR scheme was revised in 1979.<sup>4</sup> Some requirements for the main grades are given in Table 2. CV and L grades are “latex” grades, that is, prepared by direct coagulation of whole field latex. SMR5 is restricted to rubber derived from sheet material, such as RSS, which is processed and presented in the SMR block form. The lower grades SMR10, SMR20, and SMR50 originate from field grades of rubber,

**Table 1. Preservatives.**

<i>Latex Type</i>	<i>Preservative System</i>
Heat conc.	Ammonia, alkali
Centrifuged	
HA	0.7% ammonia
LA-BA	0.2% ammonia + 0.2% boric acid
LA-TZ	0.2% ammonia + 0.05% TMTD + 0.05% ZnO



Fig. 1. A bale of standard Malaysian rubber.

the number referring to the dirt content allowed in the specification. SMR GP is a general purpose viscosity-stabilized grade prepared from a blend of latex grade rubber, sheet material, and field coagulum rubber.

The plasticity retention index (PRI) is a measure of the susceptibility of the raw rubber to oxidative degradation. Oxidation is catalyzed by some metals such as copper, so that the PRI test gives an indirect indication of the presence

of such materials in the rubber. The better grades of rubber have the higher PRI.

Users of natural rubber will be familiar with the increase in viscosity and gel content which can occur during storage, an effect not surprisingly called *storage hardening*. This is particularly obvious in latex grade rubbers. The evidence suggests that the hardening is due to crosslinking associated with the presence of aldehyde groups on the rubber chain, and it can be inhibited by adding a small quantity of a monofunctional reactant for the aldehyde groups. CV rubbers are grades in which the viscosity is stabilized by the addition of about 0.15% of a hydroxylamine salt to the latex before coagulation. The hydroxylamine is not detectable in the finished rubber. In the revised SMR scheme the number of viscosity-stabilized grades has been reduced to three plus an LV grade in which the viscosity is reduced by addition of a small quantity of light mineral oil.

For use in solution adhesives, natural rubber must be masticated sufficiently to break down gel and reduce the viscosity to the required degree for dissolution in suitable solvents. As a result of their very low gel contents, viscosity stabilized rubbers dissolve without the need for mastication, although some milling may be required for other reasons. It is usual to form the rubber into a thin sheet to present a large surface to the solvent for rapid swelling. The most

Table 2. Mandatory Specifications for SMR Graded Natural Rubber.<sup>3</sup>

	SMR CV, Viscosity stabilized	SMRL, Latex	SMR 5, From sheet material	SMR GP, Blend viscosity stabilized	SMR 10 Field grade material	SMR 20
Dirt retained on 44 $\mu$ m aperture (max % wt)	0.03	0.03	0.05	0.10	0.10	0.20
Ash content (max % wt)	0.50	0.50	0.60	0.75	0.75	1.00
Nitrogen content (max % wt)	0.60	0.60	0.60	0.60	0.60	0.60
Volatile matter (max % wt)	0.80	0.80	0.80	0.80	0.80	0.80
Wallace rapid plasticity, minimum initial value ( $P_0$ )	—	30	30	—	30	30
Plasticity retention index (PRI) (min %)	60	60	60	50	50	40

**Table 3. Granulated Natural Rubber—Effect of Particle size on the Rate of Dissolution.**

<i>Particle size, expressed as diameter, mm</i>		<i>Time to reach 0.8% rubber concentration, h</i>
<i>mean</i>	<i>range</i>	
6.8	5.6–8.0	18
4.8	4.0–5.6	11
2.4	2.0–2.8	6
1.2	1.0–1.4	4
0.9	0.7–1.0	2.5

\*For a nominal 1% solution in toluene.

convenient way to achieve faster dissolution is to use one of the particulate forms now available which are produced by mechanical comminution and grinding of dry rubber.

The effect of mean particle size on the rate of dissolution is illustrated in Table 3 for fractions sieved from granulated SMR-5 bale rubber. Particles having a mean diameter of 1 mm are taken up by solvent 5–10 times faster than particles having a mean diameter of 7 mm. A rubber powder prepared from spray dried latex was marketed but proved difficult to produce. A small level of anti-tack agent such as calcium stearate is commonly used to minimize agglomeration during manufacture, and this can usually be ignored.

The advantages of CV rubbers in facilitating the preparation of rubber solutions are clear; but it should be appreciated that for a given concentration, a solution prepared from an unmasticated rubber such as a CV grade will be more viscous than when prepared from a harder rubber masticated to the same rubber viscosity (Table 4). The relationship between Mooney viscosity and solution viscosity is very depen-

dent on the temperature of mastication.<sup>5</sup> Generally, the lower the temperature of mastication to a given Mooney, the higher the viscosity of a resulting solution (Fig. 2).

### **Natural Rubber Grafted with Methyl Methacrylate (Heveaplus MG)**

A grafted copolymer (Heveaplus MG) based on natural rubber has been available for many years. In distinction to the synthetic block copolymers which have been introduced into adhesive technology, Heveaplus MG is a comb-type material having a natural rubber backbone and polymethyl methacrylate side chains.

MG 30 and MG 49 are graft copolymers containing the percentage amounts of methyl methacrylate indicated by the numbers. They are available either as latices or as solid rubbers from suppliers in Malaysia. Alternative supplies are often available from specialist manufacturers in consuming countries. Although there is always present some methyl methacrylate homopolymer, at least 50% is grafted. The latex contains 50% total solids and is easily manufactured in an adhesives factory. Table 5 gives the recipe for preparation of the latex.<sup>7</sup>

The latex form of Heveaplus is compounded in the usual way with dispersions of required additives to formulations as exemplified in a latter section. Solid Heveaplus MG is best milled on a two-roll mill to bring about some breakdown and elimination of gel material before dissolving in solvent. The degree of milling should be carefully controlled, as excessive milling will lead to the elimination of grafted material and increase the amount of homopolymer. A recommended solvent is made of

**Table 4. Concentrations of Various Rubber Types to Give Solution Viscosity of  $10^5$  Brookfield LVT units.**

<i>Rubber type</i>	<i>Mooney viscosity, ML (1 + 4) 100°C</i>	<i>Concentration required, %</i>
SMR L, masticated	45	17.5
SMR L, masticated	70	11.5
SMR L, unmasticated	95	7
SMR CV, unmasticated	65	9

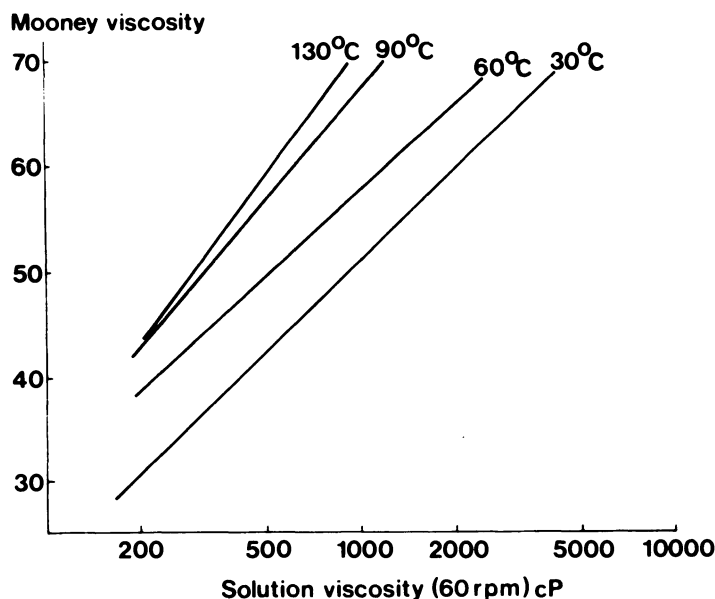


Fig. 2. Effect of mastication temperature on the solution viscosity of natural rubber (SMR5 grade, 7% solution in toluene).<sup>5</sup>

equal parts of toluene and methyl ethyl ketone. The hardness of the film deposited from solution may be varied according to the balance between nonpolar solvent favoring rubber solution and polar solvent favoring polymethyl methacrylate solubility. Solution polymerized Heveaplus MG is made from SMR or masticated pale crepe rubber, and a method suitable for a laboratory scale preparation was described in the second edition of this Handbook.

**Table 5. Manufacturing Recipe for Heveaplus MG 49.**

	Parts by wt., wet
Natural rubber latex concentrate (high ammonia, 60% rubber content)	1000
Ammonia solution (2% by wt.)	735
Methyl methacrylate monomer (stabilizer, less than 0.02% hydroquinone)	610
<i>t</i> -butyl hydroperoxide (minimum 65% active)	2.0
Oleic acid	3.0
Tetraethylene pentamine aqueous solution (10% by wt.)	8.5

### Depolymerized Rubber

This material has been available for many years in the United States<sup>8</sup> and in the UK.<sup>9</sup> It is a liquid rubber prepared by extensive mastication at high temperature (250°C) in the presence of air and a peptizing agent. A range of viscosity grades can be produced by varying the time of treatment. This material is soluble in many organic solvents but not alcohols and ketones, and is compatible with many drying oils and ester-type plasticizers. More recently, French workers have developed a method for preparing liquid natural rubber from chemically treated latex.<sup>10</sup> Although this particular method has some disadvantages, a pilot plant has been erected in the Ivory Coast to develop the process technology. Possible markets include use as a tack builder in the manufacture of tires.

Experimental work has shown that a chemically depolymerized latex exhibits the characteristics of a pressure-sensitive adhesive.<sup>11</sup> Good peel strength was found without the addition of resin, and as the low glass transition temperature of natural rubber was not affected by the reaction, these materials may be of interest in low temperature applications. Blends

with normal latex and resins gave good bonds to polythene.

### Synthetic Polyisoprene

There is no reason in principle why synthetic polyisoprene should not replace natural rubber in many of the recipes discussed later. However, there are some differences in behavior, mainly associated with the differences in molecular weight and gel, the higher content of *trans* isomer in synthetic polyisoprene, and the naturally occurring materials in the natural rubber.

On the advantageous side the gel-free nature of the synthetic material gives solubility in solvents without preliminary mastication. Set against this is the relatively poorer tack and poor green strength. For unvulcanized adhesives, therefore, the poorer performance must be set against greater ease of preparation and possibly less tendency to gel in storage.

Vulcanizing adhesives need some small changes in the recipe to allow for the fact that synthetic polyisoprene does not contain lauric acid, so that the minimum loading of stearic acid must be watched. It is also free of nitrogen compounds, so that for a given level of sulfur and accelerator a slightly softer compound is obtained, which also cures rather more slowly. Should the bond be under some stress before curing starts, tackifiers could usefully be added or increased to ensure holding the bond until vulcanization is under way. There is no reason why, in a vulcanized adhesive, fully equal performance should not be obtained.

A liquid synthetic polyisoprene is marketed by the Japanese company Kuraray.<sup>12</sup> This product, which is made by the polymerization of isoprene monomer, is available in a wide range of different viscosity and chemically modified grades. Because of its high purity, there is a significant market in surgical adhesives.

### FORMULATION OF LATEX ADHESIVES

The general principles governing the formulation of adhesives have been discussed elsewhere<sup>13</sup> and it will be assumed that the property of *tack* or *tackiness* is understood by

the reader together with underlying scientific phenomena such as thermodynamic wetting and diffusion.

Natural latex is polydisperse, i.e., the size of the individual particles varies considerably (Fig. 3) from as little as 0.01  $\mu\text{m}$  up to about 5  $\mu\text{m}$ . This is in contrast to most synthetic latex in which the range of particle size for a particular latex is quite narrow. In natural latex the greatest proportion of the particles in number terms has a diameter less than 0.5  $\mu\text{m}$  but most of the mass of the rubber is in particles greater than 0.6  $\mu\text{m}$  in diameter. As a result of the wide particle size distribution, NR latex has a very good relationship between rubber content and viscosity, so that the viscosity at a given rubber content is relatively low in comparison with synthetic latex.

In common with other high polymers natural rubber is heterogeneous with regard to molecular weight, so that any particular sample contains a range of molecular weights (Fig. 4). The average molecular weight is usually taken to be about one million. However, the picture is complicated by the presence of gel, the portion of the rubber which does not dissolve in a good solvent.

In fresh ammoniated latex the gel content is usually low, e.g., about 2% at 14 days after tapping. This may rise to about 30% by 2 months and 40–50% by 4 months. The latter figure would be typical of commercial latex by the time it is delivered to the consumer in most countries. A typical molecular weight distribution plot for commercial concentrate is shown in Fig. 4. The formation of gel is greatly inhibited in CV latex (Fig. 4), resulting in a

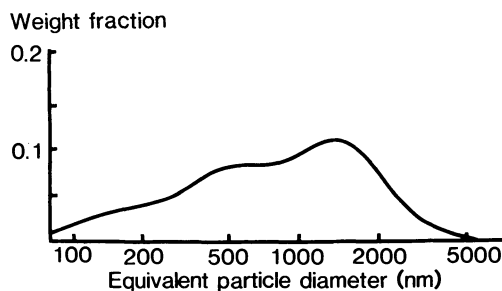


Fig. 3. Particle size distribution (weight) of a sample of NR latex obtained by Proton correlation spectroscopy (Malvern 4600 instrument).

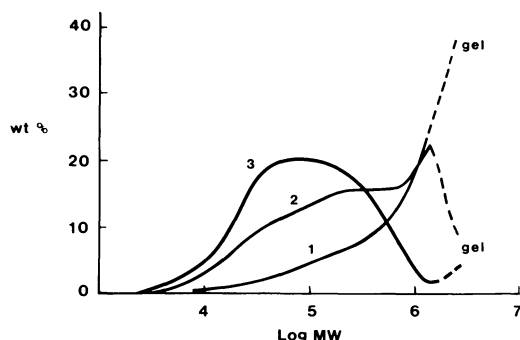


Fig. 4. Molecular weight distribution in samples of natural rubber latex: (1) HA latex; (2) CV latex; (3) depolymerized latex.

lower gel content (5–10%) and average molecular weight ( $M_w \approx 600,000$ ).

The main characteristics of normal NR latex are as follows:

1. High gel content
2. High molecular weight
3. High cohesive strength
4. Low intrinsic tack
5. High self tack
6. Low content of soap and other non-rubber materials
7. High rubber content

The relative importance of these factors varies with the application. In some cases the application may be critically dependent on one or two properties.

Latex adhesives may conveniently be divided into two types, wet bonding and dry bonding. *Wet bonding* adhesives are applied to the joining surfaces in the fluid state, the bond being formed by drying. An important feature of these adhesives is that there is an important mechanical component in the bonding process. Therefore bulk properties, such as modulus, are significant and filler addition is often used to stiffen the adhesive with a useful reduction in cost. It is essential for the development of the bond that water should be removed from the adhesive, and wet bonding adhesives are only suitable for situations in which at least one surface is water-porous, e.g., paper, leather, concrete, and textiles. Typical instances of this type are anchor coats for tufted carpets, ceramic tile adhesives, and the quick-grab adhesive described later.

*Dry bonding* adhesives are used to form bonds after the water has evaporated. They may also be classed as pressure-sensitive adhesives, because pressure is needed to achieve contact between the joining surfaces. The most simple case is the dried natural rubber latex film which will stick only to itself and requires that both surfaces be coated. At the other extreme is the material normally associated with the term pressure-sensitive adhesive, which will stick to a variety of surfaces.

In some cases bonding is carried out with the adhesive in a part dried condition, as natural rubber latex films combine very easily in this state. Further reduction in water content at the combination stage may be allowed if small quantities of a tackifying resin are added.

In many cases it will be necessary to increase the viscosity of the adhesive with thickener. Examples of this are thick bed or gap filling adhesives, or adhesives for use on porous substrates. Naturally occurring materials are sometimes used, such as karaya gum; casein also tends to increase viscosity as well as behaving as a stabilizer. However, it is now more usual to use synthetic polymers such as methyl cellulose and similar derivatives, and polyacrylates.

### Quick-Grab Adhesive

These adhesives are used in the shoe industry for bonding insoles and labels into shoes. The adhesive is applied wet, must allow adequate time for positioning, and should then set within a few seconds under finger pressure. On substrates which are reasonably porous, a natural latex with high rubber content (ca 65%) has suitable properties.<sup>14</sup> Water absorption into the substrate reduces the colloidal stability so that it becomes sensitive to the rubbing action of the finger. The time required for this can be controlled by adjusting the viscosity of the aqueous phase with small additions of thickener or water.

Although the film is still wet at this stage, the gel has sufficient strength to hold the insole in place until full strength is reached through drying. Soap addition, even at low level, tends to destroy the quick-grab action by making the latex too stable. The best material for this ap-

plication is high solids centrifuged latex; creamed latex, although of high solids content, does not behave in the same way, possibly due to residual creaming agent.

Normal concentrate can be made to behave in a similar fashion by the addition of 3–5 pphr of a swelling solvent such as toluene. This effectively increases the nonaqueous volume fraction, simulating a high solids latex. As an alternative, the stability of the latex can be reduced by treatment with a proteolytic enzyme, with very small addition of soap to adjust stability if this is found to be too low.

### Self-Adhesive Envelopes

When natural rubber latex dries, some of the soluble non-rubber components are brought to the surface by water transport and are left as a thin film when drying is complete. This tends to reduce the surface tack of the rubber so that raw latex films are generally nonadherent when pressed on to other surfaces. When the film is pressed against a similar surface, however, it is thought that the thin non-rubber layer is displaced, allowing the two natural rubber surfaces to achieve contact and form a bond, accounting for the good self tack of films from natural latex. This characteristic has led to the development of the self-adhesive envelope. The high cohesive strength of the rubber provides a security aspect by ensuring that the envelope cannot be opened without the fact being obvious through damage to the seal.

Formulation I at the end of this chapter is a suitable base. Preservation against bacterial attack is necessary, as also is a fungicide, as the dried film is open to the atmosphere. Zinc diethyldithiocarbamate performs both functions. It is sometimes found that an occasional batch of latex does not display a sufficient degree of self adhesion, and this may be overcome by adding a small amount of a high molecular weight plasticizer. A liquid polybutene added up to 10 pphr as a 50% emulsion is suitable. In some cases it may be necessary to improve the bond to the paper so that the envelope may not be opened without tearing the paper; a polyvinyl acetate latex added at about 10 pphr has been found to achieve this without noticeable loss of self tack.

### Latex Pressure-Sensitive Adhesives

Although natural rubber has good self tack, in adhesive terms its intrinsic tack is low. However, it is well known that the good tack properties required for pressure-sensitive adhesives can be obtained by compounding with tackifying resins. This technology is well established in solution adhesives based on solid rubber, and usually requires that the gel fraction be eliminated and the molecular weight be reduced to facilitate solution and for other reasons. This is done by mastication, but mastication is not possible with latex. From the compounding viewpoint this does not matter, as components are added as dispersions; but it does have some effect on the resulting adhesive.

In general, for a given composition the latex adhesive will tend to have higher cohesive strength. It will also have lower tack and will require a higher contact pressure or longer contact time to achieve the same bond strength. This is because the high molecular weight and gel phase impart a higher modulus and resilience to the adhesive, so that the adhesive is less compliant and it is more difficult to achieve good contact with a surface. Thus the latex adhesive will require the use of softer resins and/or higher levels of resin than for comparable solution adhesives prepared from solid rubber. The lower gel content and molecular weight of CV latex rubber is reflected in an increase in tack measured under low contact pressure, as shown for probe tack and the quick-stick test in Table 6.<sup>15</sup>

This trend can be developed further by chemical modification.<sup>11</sup> Fig. 4 shows the changes in molecular weight distribution which can be obtained by controlled oxidative depolymerization of the latex rubber. These materials are particularly interesting as they have intrinsic

**Table 6. Effect of Rubber Plasticity on Tack.**

	<i>HA latex</i>	<i>CV latex</i>
Wallace plasticity	95	50
Probe tack (N)	5.4	7.3
Quick-stick (N/cm)	2.9	4.3
90° Peel (N/cm)	5.4	5.2

tack, i.e., they possess pressure-sensitive adhesive properties without addition of tackifying resin (see Fig. 5). They can be blended with normal latex to improve cohesive strength (Fig. 5), with resin to improve tack or peel strength (Fig. 6), or with both as necessary.

Tackifying resins must be added to latex in the form of an aqueous dispersion. These are available commercially, although at present the choice is not as wide as with solid resins. Considerable expertise is required to formulate resin dispersions, as it is important that the particle size be small, preferably less than  $1\text{ }\mu\text{m}$  in diameter. Large particle dispersions may result in reduced tack and delay in attaining equilibrium between rubber and resin in the adhesive film. The most popular resins for natural rubber are based on rosin esters, and these may be extended with cheaper synthetic hydrocarbon resins depending on the adhesive properties

required. Generally it will be necessary to add a surfactant to maintain colloidal stability, and this requires careful consideration, as such materials can affect tack by migrating to the surface. This and other matters have been discussed elsewhere.<sup>16</sup>

### Tile Adhesives

The major part of the market for ceramic tile adhesives is held by formulations based on a filled polyvinyl acetate latex, but natural rubber latex is still used as a base, particularly where the adhesive is to perform under damp conditions. Formulations II and III give examples. Tile adhesives need to be stiffer than most other applications, and this effect is provided by the clay filler, which also reduces material costs and imparts gap filling properties. Cost may be further reduced by increasing the level of clay to 250 pphr, although performance will be reduced. The resin serves to improve bond strength and water resistance.

A suitable latex stabilizer is essential in view of the high filler content. The cellulose thickener aids spreading by retarding loss of water into concrete or other porous substrates. Zinc diethyldithiocarbamate serves the dual function of antioxidant and fungicide/bactericide, but additional biocide is advisable for use under adverse conditions.

The ingredients should be mixed in the order given. Resin and oleic acid are dissolved in the solvent and then allowed to cool. Then the alkali and casein solution is added, followed by the clay slurry, latex, and other ingredients. A water-in-solvent dispersion of the clay slurry forms initially, which inverts during the later stages of adding the slurry or latex. Thickener is added to give the required viscosity. It should be noted that the conventional technique by which resin and filler are added to a stabilized latex gives a lower bond strength, and inferior spreading characteristics. This formulation in a  $50 \times 50\text{ mm}$  lap bond between tile and concrete gave a shear force of 440 N when tested wet after 7 days immersion in water. In a similar test using a commercial PVA-based adhesive, the tile fell off on removal from the water. A cheaper, solvent-free mix is given in formulation III; it uses a liquid coumarone resin

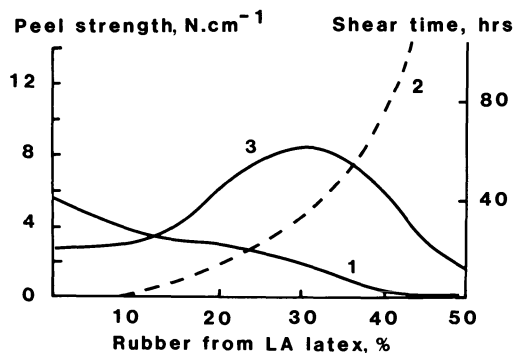


Fig. 5. Blends of depolymerized latex with normal NR latex.  $M_w = 160,000$ . (1)  $180^\circ$  Peel strength on glass; (2) hold time, PSTC7, 500 g; (3)  $M_w = 80,000$ ,  $180^\circ$  peel strength.

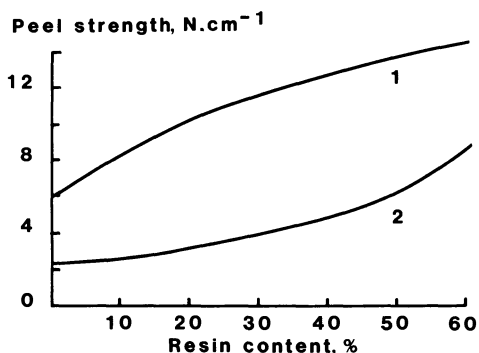


Fig. 6. Blends of depolymerized latex ( $M_w = 160,000$ ) with aliphatic hydrocarbon resin.  $180^\circ$  Peel strength tested against (1) glass, (2) polythene.



which disperses directly into the clay slurry with stirring.

A similar style of adhesive is shown in Formulation IV for wet bonding vinyl tiles to concrete, etc. In this case a softer adhesive with greater peel resistance is required. To this end the amount of filler is reduced and the resin is increased, which also improves tack. Additional softening comes from the oil. Some filler is retained to give some gap-filling ability for minor variations in substrate level. The preparation is broadly similar to Formulation II. Resins, oil, and oleic acid are dissolved in the solvent with heating and allowed to cool. The alkali and half of the casein are added to the solution with stirring, followed by the water. The remaining casein is added to the latex before adding this to the mix. The clay may be added dry or slurried first with some of the water. Vinyl-to-vinyl adhesion for a  $75 \times 35$  mm overlap joint tested in shear was 300 N for a 7-day-old bond, and the peel force was 19 N.

### Reseal Adhesives

This is a type of envelope adhesive which has characteristics enabling the flap to be sealed and unsealed several times. The main requirements are the ability to make a good bond to the paper or other substrate and good cohesive strength so that the adhesive is not distorted during the unsealing action. As the adhesive is applied to each joining surface only a limited degree of tack is necessary. Formulation V has these characteristics. The resin suggested, which has a high degree of aromatic structure, promotes the bond to difficult substrates without imparting too much tack. The clay and prevulcanized latex improve cohesive strength and also control surface tack.

The balance between tack and cohesive strength may be varied by the balance between unvulcanized and prevulcanized latex. The prevulcanized latex should be clarified after prevulcanization, i.e., centrifuged to remove excess vulcanizing components. This is to prevent post-cure in the adhesive, which may reduce tack too much.

### Anchor Coat for Tufted Carpets

Tufted carpets are manufactured by looping the yarn, which forms the pile through a textile

base. The pile is locked into position by applying a coat of adhesive, called the *anchor coat* or *primary backing*, to the back of the carpet. In carpets with a secondary backing this adhesive is also used to laminate a layer of textile such as hessian to improve the structural stability of the carpet. Modern practice is to use a non-vulcanizing compound for these adhesives; Formulation VI is suitable for use with natural rubber latex. As the action of the adhesive is essentially mechanical, a high modulus is required and this is provided by the stiffening effect of a high filler loading. Further stiffening giving improved bond strength can be obtained by adding 30 pphr MG49 latex. In some cases a soft "hand" is required, and this can be met by reducing the filler content to about 100 pphr.

Low ammonia latex (LA-TZ) is preferred because of its higher inherent mechanical stability. The preferred surfactant is a salt of an alkylaryl polyether sulfate with a polyether chain length of 8–10 ether units, which is resistant to the multivalent cations sometimes found in association with fillers. Good protection against aging is given by the combination of thiourea and conventional antioxidant. For specifications which require a temperature above  $100^{\circ}\text{C}$  for an aging test, the conventional antioxidant should be of the *p*-phenylenediamine type, e.g., UOP26. Tetrasodium pyrophosphate aids dispersion of the filler and also has a beneficial effect on mechanical stability.

The components of the mix should be added in the order given, the filler being added slowly with stirring to avoid localized dehydration of the latex resulting in the formation of coagulum. Thickener is added to adjust the viscosity as required and to avoid inconsistency due to entrained air; this is best done after the air has been allowed to come out. Anchor coats of this type give a face pull tuft bond strength of 60 N or more.

### Other Nonvulcanizing Latex Adhesives

Latex adhesives are widely used in the shoe industry; one instance, the quick-grab adhesive, has already been described. Another example is found in the manufacture of canvas shoes. The base of the canvas upper is dipped into a

bath of natural latex to a depth of about two centimetres and dried. The resulting film of rubber, having impregnated the canvas, forms a mechanical bond and provides a surface with good green tack to which a rubber sole may be attached and bonded in a subsequent oven cure. Formulation VII is suitable. It is not necessary to add vulcanizing ingredients, as these diffuse across the interface from the sole compound.

Another use of latex in shoe manufacture is leather bonding, where there is often a need for a temporary support to assist positioning while the leather shapes are stitched together. An adhesive with good self tack is required. As some leathers contain heavy metals, particularly chromium, adequate protection is necessary against their effect in promoting oxidation; this could cause undue softening of the rubber and result in defacement of the leather by bleed-through. For unvulcanized rubber adhesives the best protective systems are based on metal complexing agents such as EDTA and zinc diethyldithiocarbamate. For more sensitive applications involving larger areas, as in ladies fashion boots, a prevulcanized latex is preferred (Formulation VIII).

Internal trim for automobiles may be conveniently secured by a latex adhesive which must be light colored and protected against oxidation by a nonstaining antioxidant. Some thickener and tackifier is desirable, as much of the trim is fabric and penetration through this would constitute a serious fault. Formulation IX aims at meeting these properties.

Latex compounds are used as sealants in various types of metal containers, including ordinary cans, drums, and pressurized aerosol cans. The latex is applied as a wet layer to the end-plates and dried and cured. When the plate is sealed to the body of the can the latex deposit acts as a seal. As cans are commonly used in food contact applications, the formulation must be chosen with care and be based on HA latex. Formulation X is an example. It should be ensured that in food contact applications the compound complies with local regulations, which vary from country to country.

Similar comments apply to crown cork adhesives. These are used in crown cork closures to secure the thin layer of cork to the waxed paper in contact with the liquid or the metal cap. Formulation XI is typical of the material

used for this purpose. It is free from fillers but contains preservatives; for, although it is not in direct contact with biologically active liquid, mold growth could develop.

### Vulcanizing Latex Adhesives

The major use of vulcanizing latex adhesives is in the manufacture of textiles, rugs and carpets, and closely allied products such as rubberized hair. As in many other latex applications, ultra-accelerators are used to effect vulcanization. The materials used must be stable in alkaline dispersions, although they need not be active, since if the alkali is ammonia it will normally be removed early in the drying/vulcanization process. The vulcanization ingredients, sulfur, zinc oxide, and the insoluble accelerators must be added as dispersions in water, and these are conveniently prepared at 50% solids and stabilized by an anionic surfactant. Such dispersions may be made by ball-milling or may be easily purchased premade from specialist suppliers. Soluble accelerators can be added as solutions directly to stabilized latex, but the solutions have a much more limited life than do dispersions.

To obtain vulcanization at room temperature, combinations of accelerators are often used. The most effective for general use is zinc dibutyldithiocarbamate (ZBUD) and a thiazole such as zinc mercaptobenzthiazole (ZMBT). Typical levels are 1 pphr together with 1–1.5 pphr sulfur. The use of the sodium salt of the dithiocarbamate should give some increase in activity. Several manufacturers supply low temperature accelerators based on activated dithiocarbamates in which the zinc is complexed by an organic amine. In most instances room temperature curing systems are not required, as temperatures suitable for normal curing systems are used in the drying oven; cure takes place during and as an extension of the drying stage. For these cases a conventional system of dithiocarbamate, zinc oxide, and sulfur is satisfactory, e.g., 1 pphr of each. Modulus can be boosted by 1 pphr ZMBT if required.

It should be realized that many latex vulcanizing systems are more active in wet latex than in the dry film, and will prevulcanize the latex over a period of one to two weeks, particularly in regions having high ambient temperatures.

This may alter the characteristics of the adhesive; for example tack will be lower even if tackifying resin is present. Where prolonged storage is envisaged a two-part compound may be necessary, with the accelerator and sulfur separated. As an alternative, an accelerator system based upon zinc dibenzylthiocarbamate may be used, as this is much less active in ammoniated latex.

The increase in modulus produced by vulcanization is useful where the adhesive bond has an important mechanical component, as the need to add filler for stiffness is reduced. Filler is sometimes included to reduce cost, but the amount may be limited by the higher performance requirements of those applications in which vulcanizing adhesives are often used. An example of this is Formulation XII for anchor coat backing of washable rugs and bathroom mats.<sup>17</sup> The highly filled unvulcanized adhesives of Formulation VI would not stand up to the repeated washing to which such articles are subjected. In this compound choice of antioxidant is particularly important for adequate aging/washing resistance.<sup>18</sup> This formulation requires drying/curing conditions of about 15 mins at 130°C.

Nonwoven fabrics are usually prepared by forming a uniform web of fibers to which a bonding agent is applied by spray or impregnation. Natural rubber latex has been displaced from much of this market by special purpose synthetic polymer dispersions but is still preferred where mechanical properties, particularly resilience, are important. Examples are carpet-underlay felts and low density shoe insole felts. A general purpose formulation for this purpose is shown in Formulation XIII. A suitable stabilizer is a sulfated alkylaryl polyether surfactant. As waste fibers are often included in nonwoven fabrics, the antioxidant should give good protection in the presence of copper.

A preservative such as lauryl pentachlorophenate may also be included, and a deodorant for insoling. A cure of 3–8 minutes at 120°C in hot air is suggested.

Natural rubber latex is also the preferred binder for rubberized hair/coir products. In these materials, which are used for packaging and upholstery, resilience is particularly im-

portant. Formulations XIV and XV differ only in the sulfur level. Some sulfur combines with animal hair and extra is needed to give the degree of vulcanization required for low compression set and good resilience. Intermediate levels should be used for hair/coir blends. Application rates may vary from 10 to 100% of the weight of the fiber depending on the end use. The sprayed fiber pads should be dried at 60–70°C and cured 30 min at 100°C in hot air. Low ammonia (LA-TZ) latex is preferred for its better mechanical stability. An efficient antioxidant is needed to protect the thin films of rubber which bind the intersections of the fiber.

An unfilled gum adhesive is also suggested for bonding the two-part fabric covers to the inner core of tennis balls. In common practice a solution adhesive has been used, but a switch to natural rubber latex can avoid the problems arising from the use of solvents. A simple compound based on a stabilized latex with vulcanizing system can be used but tends to be sensitive to the degree of drying given before bonding, i.e., poor bonding may occur if drying is taken too far. The addition of a minor proportion of tackifying resin as in Formulation XVI eliminates this problem without the coated surfaces becoming difficult to handle. The ball and the covers are coated with adhesive and dried for about ten minutes at 70°C, when the covers can be applied. A dry rubber type of curing system is used to prevent the latex pre-vulcanizing and to be compatible with the higher temperatures used for vulcanizing the core.

The final example is a flocking adhesive for latex rubber gloves (Formulation XVII). Latex gloves are manufactured by the coagulant dipping process in which a layer of coagulant is left on the former when it is immersed in a solution of calcium nitrate. When the former is dipped into a suitable latex compound, a layer of latex gel forms, which is removed after drying and vulcanizing. Domestic gloves are frequently made with a flocked inner surface to produce a soft, warm feel, at the same time making the glove easier to put on the hand. The flock cannot be applied to the latex gel, so an intermediate layer of wet latex is used. For the flock to bond, the adhesive must be fluid, and a nonionic surfactant is used to stabilize the ad-

hesive against the gelling action of calcium ions which diffuse through the gel deposit. The viscosity is increased to 200–300 cp (Brookfield LVT Viscometer, spindle 2, 60 rpm, 23°C) by the addition of a thickener so that sufficient adhesive is picked up on the gel to anchor the flock.

## SOLUTION ADHESIVES FROM NATURAL RUBBER

### Nonvulcanizing Adhesives

For many purposes a simple solution of rubber in a solvent gives a useful adhesive. This is particularly so for natural rubber, which is tacky without the need for tackifying resins. However, the adhesives of commerce are much more sophisticated and achieve their superior results by the careful matching of additives and solvents to intended applications. The principal additives in use today are described here.

*Tackifying Resins.* These are advantageous when the dried surface of the adhesive is intended to be permanently tacky, as with a pressure-sensitive tape, or at least to remain tacky for a long while after removal of solvent. Various naturally occurring resins and their derivatives are used, such as rosin and rosin esters, terpene, and coumarone and coumarone-indene. Resins synthesized from petroleum are widely used, often in combination with those from biological sources.

*Softeners.* Unless excessively masticated, the rubber may be too hard for the application, so softeners are employed. Examples are lanolin, used for surgical plasters, and liquid polybutenes.

*Reinforcing Agents.* To increase the cohesive strength of an unsaturated rubber adhesive, carbon black is the material of choice. It must be added to the rubber in an internal mixer or on a two roll mill before the rubber is dissolved in the solvent. Such additions do, of course, stiffen the dried adhesive, and some softener may be required to balance this, though this could adversely affect adhesive performance. Carbon black used to be added by means of whole tire reclaim but, as noted in the introduction, the practice is declining.

A different type of reinforcement is achieved by the use of polyfunctional isocyanates. As

these produce a degree of crosslinking, it would be more logical to include adhesives using them in the section on vulcanizable solution adhesives. However, there are differences which affect their formulation as well as their properties. Like vulcanizing solution adhesives, those reinforced by isocyanates must be supplied as two-part compounds mixed immediately before use. However, in the present case, one part is identical in composition with a typical nonvulcanizing solution adhesive and the other is a simple solution of the polyisocyanate. Moreover, curing is always at room temperature. As is well known, isocyanates react readily with water and other compounds with active hydrogen. Hence special care must be taken to use dry solvents and in particular to avoid the use of the tailings from tanks of hydrocarbon solvents. When mixed solvents are used, alcohols must be absent. The crosslinking of natural rubber by isocyanate occurs at the few hydroxyl groups introduced adventitiously during preparation or mastication of the rubber. Isocyanate may also react with the substrate on which the adhesive is spread.

Chlorinated rubber is also a valued reinforcement agent for natural rubber adhesives, improving the cohesive strength of all adhesives formulations and the adhesive strength to many substrates.

*Antioxidants.* The use of an antioxidant at about 1 phr or as recommended by the supplier is always to be recommended with natural rubber except for surgical applications. Care must be taken with the choice, bearing in mind the possibility of migration to the substrate.

*Fillers.* Apart from carbon black, fillers do not play a large part in the formulation of solution adhesives. Small additions of clay or whiting are sometimes used to control viscosity, but usually this is achieved by solvent blending. An exception to this is the traditional use of zinc oxide in surgical plasters and tapes and of whittings or clays where there is a need for some gap-filling property. Solvent adhesives are not, in essence, good gap fillers, however.

Formulations XVIII–XX illustrate the relatively high resin content required by permanently tacky, pressure-sensitive materials. In

Formulation XX the high filler content option would tend to be used with a high resin content, and certainly the very high loading of zinc oxide would now be regarded as extravagant for a commercial tape.

Formulations XXI–XXIII would at one time have been used domestically in the do-it-yourself market. Most adhesives now in this market are highly polar synthetic materials, which are preferable for securing decorative laminates to wooden and plaster substrates; but for many purposes about the home such as securing paper, waterproof labeling, or repairing leather or rubber articles, this series of adhesives could be used.

The general-purpose black adhesive of Formulation XXII could be used for amateur repairs to car trim, securing car mats and vibration damping which has become detached, although where appreciable engine warmth is experienced Formulation XXIII would be preferable. The latter compound could also be used in black leather footwear manufacture and in the assembling of rubber boots. Formulations XXII and XXIII both contain whole tire black reclaim, and for many purposes they could with economic advantage be formulated with further reclaim replacing the new rubber. If this revised formulation is attempted, the coumarone resin could be usefully replaced with 50 parts of wood rosin or zinc resinate to provide a higher acid number to assist solution of the reclaim.

Such reclaimed rubber adhesives are suitable for packaging, fitting padding in ammunition boxes, canvas-to-wood, and for making kraft papers. They can also be used, if necessary, with small additions of softeners, as gunnable adhesives, and on building sites for securing wall panels.

### Vulcanizing Adhesives

Unlike vulcanizing latex adhesives, which have a storage life measured in weeks, vulcanizing solution adhesives have a limited pot life and are stored as two-component mixtures. The two parts are mixed immediately before use and the solution will then have a workable life of perhaps 2–4 hours before gelation occurs. It is usual to formulate the two parts with the sulfur

and one-half the rubber content in one solution and the accelerator and remaining rubber in the other half.

An important consideration is that two solutions of comparable kinematic viscosity are more easily mixed than two which differ markedly. Comparable kinematic viscosities are most easily obtainable by arranging density and viscosities to be equal. This is illustrated in Formulation XXIV. This compound is a self-vulcanizing cement such as might be used for joining proofed fabrics. Formulation XXV would serve the same purpose.<sup>19</sup> For joining heavy duty proofed fabrics such as panels for hovercraft skirts and the like, a much more sophisticated compound would be used containing tackifying resins, a substantial quantity of carbon black, and polyisocyanate as well as vulcanizing ingredients. However, because of the gelling reaction with rubber, the polyisocyanate would be added separately just before use so that, in effect, a three-part compound would be involved. The isocyanate might also be mixed into a solution of chlorinated rubber, where it would have a reasonable pot life.

Formulation XXVI is a two-part compound suggested as suitable for bonding vulcanized rubber to vulcanized rubber.<sup>20</sup> After curing for 7 days at room temperature the peel strength of laminated NR strips was 1.8–2.8 N/mm depending on the nature of the rubber strips. Details of performance under the other conditions are given in Ref. 20.

### Mastics, Asphalts, and Sealants

Mastics are sealing materials which adhere to the substrate and are used as fillers in metal or brickwork corners and angles. They are usually of high viscosity and become effectively immobile on loss of solvent or water, the shrinkage occurring wholly from the free surface. Frequently such materials contain drying oils or bituminous components which harden with time and form a skin over the surface. Asphalts are used in the preparation of waterproof building and packaging papers in which coarse grade papers are bonded together by the impermeable asphaltic layer. They are also used extensively in roads and sidewalks (pavements), and repairs to them are made with an

asphaltic mass, the adhesive properties of which are greatly improved by the addition of small quantities of rubber. Natural rubber, usually in the form of latex or a dispersion of reclaimed rubber, is used as an additive to bitumen sealants used in the construction of concrete roads. The rubber improves both adhesion to substrate and low temperature flexibility. A typical general asphaltic-reclaim compound is given as Formulation XXVII. Palinchak and Yurgen<sup>1</sup> have given details of the preparation in which the compound is formulated from dry components into which water is mixed and alkali added to invert from a continuous rubber phase to a continuous water phase, followed by addition of the asphalt dispersion and clay slurry. Formulation XXVII could form the basis of a wide variety of adhesive compounds tailored to particular end uses. For the manufacture of draft-type papers a lower level of asphalt might be desirable, while for mastic-like usage the level of clay could be considerably increased, with a reduction in the water content.

In any use the addition of 2.5 parts of casein on 100 of reclaim would be expected to improve the compound. A road repair compound is illustrated in Formulation XXVIII. This rubber is conveniently added to the heated asphalt in the form of powdered rubber. Control of the heating process is very important, as overheating degrades the rubber. High molecular weight is essential in the long-chain polymer component, and hence new natural rubber of good quality rather than reclaimed rubber is desirable.

### GRAFTED COPOLYMER HEVEAPLUS MG

The natural rubber adhesives, particularly when vulcanized, perform best with essentially non-polar adherends or those where a strong mechanical element is involved in the adhesion mechanism. Adhesion to smooth polar surfaces suggests a polar adhesive, and when this requirement conflicts with other requirements for which a nonpolar adhesive is preferable, it is common practice to prime coat the adherent surface with a polar material which is also compatible with the nonpolar adhesive. An ef-

ficient way of priming polar surfaces for the reception of natural rubber adhesives is by use of Heaveaplus MG, the preparation of which has been outlined previously.

As a primer coat on polyvinyl chloride (PVC) backed adhesive tape, Formulation XXIX is prepared either directly by grafting in the solvent, or by masticating solid graft polymer to a suitable consistency, adding the filler on the mill, and then steeping in solvent. The methacrylate graft proportion can be adjusted to the desired figure by mixing two materials of higher and lower methacrylate content. The titania is optionally added as a marker to assist identification. The solvent is conveniently made of equal volumes of methyl ethyl ketone and toluene. As a priming solution for synthetic upper materials when natural rubber soling is to be molded directly it is recommended that accelerator be added to the adhesive solution; sulfur will migrate in adequate quantity to ensure vulcanization. The accelerator may be the same as that used in the soling, if this is known, otherwise up to 3 pphr piperidinium pentamethylene dithiocarbamate may be used.

An MG latex has been suggested as an adhesive for bonding a woven synthetic fabric such as polyester to EPDM.<sup>21</sup> It was necessary to clean the surface of the EPDM by solvent or scouring using wire wool and soap solution. A wet bonding technique with MG10 latex gave the best results with cohesive failure in the EPDM.

### ACKNOWLEDGMENT

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### FORMULATIONS

These formulations are indicative of the general principles and order of quantities and it should not be assumed that they can be made without modification to suit the circumstances and materials of manufacture of particular applications for which they are intended. All formulations are based on parts by weight.

Adjustment should be made for concentrations or solids content differing from those stated.

## I. Self-Adhesive Envelopes

60% Natural latex	167
10% Potassium hydroxide solution	0.2
50% Aqueous dispersion of zinc diethylthiocarbamate	1.0

## II. Ceramic Tile Adhesive

Hydrocarbon resin (60% soln in toluene)	167
Oleic acid	3
5% Potassium hydroxide	15
15% Casein	20
65% Clay slurry	232.5
60% NR latex	167
Cellulose thickener	3-4
Water	10
50% ZDC	2
10% Thiourea solution	10

## III. Ceramic Tile Adhesive

65% Clay slurry	232.5
Pale liquid Courmarone resin	100
Polyethoxy sulphate stabilizer (30% active)	15
60% NR latex	167
Cellulose thickener	3-4
50% ZDC	2
10% Thiourea solution	10

## IV. Adhesive for Bonding Vinyl Tiles to Concrete

Terpene-phenolic resin <sup>a</sup>	100
Pale liquid coumarone resin	50
Process oil <sup>b</sup>	50
Oleic acid	22.5
Solvent <sup>c</sup>	25
10% Potassium hydroxide solution	40
15% casein solution	20
Water	75
50% Zinc diethylthiocarbamate dispersion	4
60% NR latex, HA or LA-TZ type	167
Clay	100
Cellulose thickener <sup>d</sup>	as required

a. e.g., SP 560 (Schenectady).

b. Aromatic oil, e.g., Dutrex 729 (Shell).

c. White spirit or other suitable solvent.

d. High viscosity type, e.g., Celacol HPM 5000 (British Celanese) or Methofas PM 4500 (ICI).

## V. Resealable Adhesive

LA-TZ latex (60%)	111
LR Revultex (60%)	56
10% Ammoniated casein	20
Dresinol 902, 45% TSC (Hercules)	220
Devolite clay	40

## VI. Tufted Carpet Anchor Coat Adhesive

60% NR latex, LA-SPP	167
25% Surfactant solution	3
Tetrasodium pyrophosphate	1
Water (to 72-75% total solids content)	as necessary
Filler, e.g., whiting	400
10% Thiourea solution	10
50% Antioxidant dispersion	2
Antifoam agent	as necessary
10% Thickener solution (polyacrylate)	4

## VII. Canvas Shoe Sole Adhesive

60% NR latex (LA-TZ type)	167
50% Titanium dioxide dispersion	10-20

## VIII. Leather Adhesive

60% Natural latex	167
Sodium ethylenediaminetetraacetate, 20% soln.	2.5
Antioxidant, e.g., polymerized trimethyl hydroquinoline as 50% dispersion	1

## IX. Automobile Internal Trim

60% Natural latex	167
5% Methyl cellulose	40
50% Antioxidant (as 50% dispersion)	4
50% Clay dispersion	100
50% Coumarone-indene dispersion	20
Coloring to give drab or neutral color or as required.	

## X. Can Sealant

NR latex, 60% rubber, HA type	167
10% Casein solution	10
50% Food-grade antioxidant dispersion	2
66% Clay slurry	167
5% Thickener solution	5

## XI. Crown Cork Adhesive

60% Natural latex	167
Fungicide	0.2
Ammonium caseinate, 25% aq. sol.	11.2
Sodium hydroxide, 25% sol.	0.40
Formalin, 40% aq. sol.	5.10
Rosin ester, dispersion	10

## XII. Washable Rug Anchor Backing formulation

60% NR latex, LA-TZ type	167
25% Surfactant solution	3
Filler, e.g., whiting	50
50% Zinc oxide dispersion	6
50% Sulfur dispersion	4
50% Zinc diethylthiocarbamate dispersion	2
50% Zinc 2-mercaptobenzothiazole dispersion	2
50% Antioxidant dispersion (e.g., 2246)	2
10% Thickener solution	10
	or as required }

## XIII. General-Purpose Adhesive Binder for Nonwoven

## Fabrics

60% Natural rubber latex	167
20% Stabilizer solution	2
50% Sulfur dispersion	4
50% Zinc diethyldithiocarbamate dispersion	3
50% Zinc 2-mercaptobenzothiazole dispersion	1.5
50% Antioxidant dispersion	2
50% Zinc oxide dispersion	6
Soft or distilled water to adjust total solids	as required

Suggested cure 3–8 min at 120°C in hot air

## XIV and XV. Binders for Animal Hair and Coir

	Animal hair, XIV	Coir, XV
60% Natural rubber latex	167	167
25% Stabilizer solution <sup>a</sup>	4	4
20% Potassium hydroxide solution	2	2
50% Antioxidant dispersion <sup>b</sup>	3	3
50% Zinc diethyldithiocarbamate dispersion	2	2
50% Zinc 2-mercaptobenzothiazole dispersion	3	3
50% Sulfur dispersion	8	5
50% Zinc oxide dispersion	10	10
Water (to 50–55% total solids content)	as necessary	

a. A sulfated alkyl phenol-ethylene

b. Polymerized 2,2,4-trimethyl-1,2-hydroquinoline, e.g., Flectol H (Monsanto).

## XVI. Adhesive for Tennis Ball Covers

60% Natural latex (LA-TZ) type)	167
20% Nonionic stabilizer	3
Dresinol 303 (Hercules)	66
50% Sulfur	4
50% Zinc oxide	2
50% ZMBT	2.4
50% Titanium dioxide	8
50% Antioxidant 2246	2
Thickener (polyacrylate)	as required

## XVII. Flock Adhesive Formulation

60% Natural rubber latex	167
20% Stabilizer solution	2.5
10% Potassium hydroxide solution	2
50% Sulfur dispersion	2
50% Zinc diethyldithiocarbamate dispersion	2
50% Zinc oxide dispersion	2
50% Antioxidant dispersion	2
Antifoaming agent	0.1
10% Thickener solution	2
	or as required

## XVIII. Surgical Tape Adhesive

Natural rubber	100
Colophony or ester Gum	100
Lanolin	20
Zinc oxide	50

## XIX. Industrial Pressure Sensitive Tape A

Natural rubber (pale crepe)	100
Poly( $\beta$ -pinene) resin, mp 70°C	75
Colorless petroleum oil	5
Polymerized trimethyldihydroquinoline	2

## XX. Industrial Pressure Sensitize Tape B

Natural rubber	100
Coumarone-indene resin (35°C)	30–150
Antioxidant	1.5
Calcium carbonate or zinc oxide	30–150

## XXI. General Purpose Transparent Adhesive

Natural rubber	100
Rosin, water white grade	10
Antioxidant	1

## XXII. General Purpose Black Adhesive

Natural rubber	100
Whole tire reclaim	100
Coumarone resin	50
Whiting	50
Antioxidant	1.5

## XXIII. General Purpose Black Adhesive with Better Heat Resistance

Natural rubber	100
Whole tire reclaim	100
Zinc resinate	50–80
Clay	50
Antioxidant	1.5
together with, in separate solution,	
Polyisocyanate	10

## XXIV. Vulcanizing Cement

	Part A	Part B
Natural rubber	100	100
Sulfur	2	—
Butyl Zimate	—	7
Zinc oxide	20	—
Antioxidant	5	—

## XXV. Fabric Combining for Double Texture Waterproof

	Part A	Part B
Natural rubber	100	100
Zinc oxide	10	—
Sulfur	8	—
Zinc isopropyl xanthate	—	4

## XXVI. Two-Part Adhesive for Vulcanized Rubber

	Part 1	Part 2
Natural rubber (SMR 5)	100	100
Zinc oxide	5	5
Stearic acid	0.5	0.5



Antioxidant <sup>a</sup>	1	1
Accelerator <sup>b</sup>	—	1.5
Accelerator <sup>c</sup>	—	0.5
Sulfur	4	—

a. Phenol condensation product

b. Zinc isopropyl xanthate

c. Diethylammonium diethyldithiocarbamate

#### XXVII. Reclaimed Rubber Dispersion with Asphalt

Whole tire reclaim	100
Surfactant	2-5
Caustic potash	1-2
Ester gum	20-30
Clay	30-40
Asphalt emulsion	175-185
Water	70-80

#### XXVIII. Road Repair Compound

Natural rubber (powder)	1
Asphalt	60
Fine aggregate consisting of broken stone of small size mixed with sharp sand	34

#### XXIX. Heveaplus MG Primer for PVC

Heveaplus MG	5
Titanium dioxide (optional)	0.1
Solvent	to 100

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# Butyl Rubber and Polyisobutylene

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## INTRODUCTION

Butyl rubber and polyisobutylene are elastomeric polymers<sup>1</sup> used quite widely in adhesives and sealants both as primary elastomeric binders and as tackifiers and modifiers. The principal difference between these polymers is that butyl is a copolymer of isobutylene with a minor amount of isoprene, which introduces unsaturation, while polyisobutylene is a homopolymer.

Butyl rubber, as shown in Fig. 1, has a relatively long and straight carbon-hydrogen backbone, containing between 47,000 and 60,000 units. This regular structure, with few double bonds or reactive sites, renders butyl very stable and quite inert to the effects of weathering, age, and heat. It has good resistance to vegetable and animal oils and to attack by chemicals. Being an all-hydrocarbon material, the butyl polymer has a very low water absorption and is soluble in typical hydrocarbon solvents. The many side groups attached to the polymer chain produce a high degree of damping. Since these side groups are not large in size and are regularly spaced, close, unstrained molecular packing results. This characteristic leads to the unique low air, moisture, and gas permeability of this polymer.

The polyisobutylene polymers have a chemical backbone similar to butyl rubber, but they

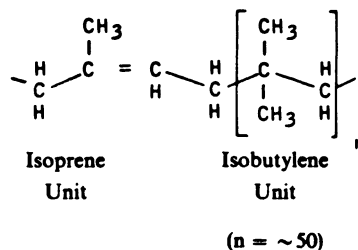


Fig. 1. Butyl rubber molecule.

are essentially free of double bonds in the polymer chain (they have only terminal unsaturation). Many of their characteristics are similar to butyl, e.g., age and chemical resistance, very low water absorptivity and low permeability. The polyisobutylenes are produced over a wider molecular weight range than butyl. The low molecular weight grades are soft, tacky, water-white semi-liquids, while the higher molecular weight grades are strong, tough, elastic rubbers.

Polymers of the isobutylene family (i.e., butyl and polyisobutylene) have very little tendency to crystallize and depend upon molecular entanglement or crosslinking for their strength, rather than upon crystallinity. The completely amorphous character of these polymers gives an internal mobility which imparts flexibility, permanent tack, and resistance to shock. Their low glass transition temperature,  $-60^\circ\text{C}$ , in-

icates functional properties such as flexibility are maintained at temperatures considerably below ambient. Since these polymers are hydrocarbons with no or very little polarity, even though their tack is high, their chemical attraction to many surfaces is weak and therefore they are often mixed with resins and materials which impart some polar character to the blend. Polyisobutylene polymers possess very good dielectric properties and electrical stability.

The physical, chemical, and compounding properties of the isobutylene family of polymers will vary with molecular weight, amount of unsaturation, the minor constituents in the polymer and, in certain instances, chemical modification. With proper allowance for gross differences in molecular weights, butyl and polyisobutylene can often be used interchangeably in cement and adhesive compositions that will not be cured.

Butyl rubbers are also available in halogenated form, as a low molecular weight semi-liquid, as a latex, and in various modified and

partially crosslinked forms. The grades of butyl rubber and polyisobutylene available commercially from Exxon Chemical Company are listed in Table 1. In addition to those shown, various grades of butyl rubber and halogenated butyl rubber are supplied by Polysar Limited, and of polyisobutylene by BASF.

## BASIC PROPERTIES

### Butyl Rubber

All grades of regular butyl rubber are tacky, rubbery, light amber colored solids, manufactured by copolymerizing isobutylene with less than 3% isoprene. Double bonds introduced into the macromolecule by isoprene permit the polymer to be crosslinked or vulcanized. Though butyl rubber is "unsaturated" relative to polyisobutylene, its 0.8–2.1 mole % unsaturation (number of isoprene units per hundred monomer units in the polymer chain) is still far less than the 100% unsaturation of natural rubber or the 60–80% unsaturation of SBR. This

**Table 1. Commercial Grades of Butyl Rubber and Polyisobutylene Polymers.**

<i>Grade</i>	<i>Approx. Viscosity Average Molecular Weight</i>	<i>Approx. Isoprene Units/ 100 Monomer Units (Mole % Unsaturation)</i>	<i>Comments</i>
Vistanex® LM-MS	44,000	0	Semi-liquid, tacky polymers used mainly as tackifiers
LM-MH	53,000	0	
LM-H	63,000	0	
Exxon Butyl 065	350,000	0.8	Widely used in caulks and sealants
165	350,000	1.2	Specialty uses
268	450,000	1.6	Used for high cohesive strength
269	450,000	1.6	Highest viscosity/cohesive strength grade
365	350,000	2.1	Used in curing applications
077	425,000	0.8	Special BHT stabilized FDA grade
Chlorobutyl 1065	350,000	1.9	Contain approximately 1.2 wt % chlorine
1066	400,000	1.9	
1068	450,000	1.9	
Bromobutyl 2222	375,000	1.6	Contain approximately 2.0 wt % bromine
2233	400,000	1.6	
2244	450,000	1.6	
2255	450,000	1.6	
Vistanex MM L-80	900,000	0	Lowest viscosity of MM grades
MM L-100	1,250,000	0	Widely used in PSA's
MM L-120	1,660,000	0	Widely used in PSA's
MM L-140	2,110,000	0	Highest viscosity of MM grades

Specific Gravity: 0.93 Bromobutyl; 0.92 all other grades.

All above grades manufactured by Exxon Chemical Company; butyl and halobutyl polymers are also available from Polysar Limited and polyisobutylene polymers from BASF.

purposely limited functionality of butyl rubber accounts for its excellent resistance to environmental attack.

The various butyl grades differ in mole % unsaturation, molecular weight, and nature of the stabilizer incorporated during manufacture to prevent degradation. A minor amount of metallic stearate is also added to the rubber to prevent agglomeration of polymer particles during the manufacturing process.<sup>2,3</sup>

The stabilizer used in Exxon butyl rubber is the "nonstaining" zinc dibutyldithiocarbamate. Stabilizer content is in the 0.05–0.20 wt % range. A BHT (butylated hydroxytoluene) stabilized grade of butyl is also available for applications requiring broader FDA regulation. Nonstabilized butyl is produced for special applications.

In addition to the grades of Exxon butyl rubber described in the table, a series of butyl grades is marketed by Polysar Limited, designated Polysar Butyl 100, Polysar Butyl 301, etc.

Low molecular weight, semi-liquid analogs of butyl rubber are also commercially available. One such product series is Kalene, marketed by Hardman Inc. (Belleville, NJ).<sup>4</sup> These polymers are 100% solids (free of solvent or extenders) products with viscosity in the range of one million centipoises. They can be cured through their unsaturation at elevated or room temperatures to enhance cohesive strength. Low molecular weight butyl can be easily compounded into high solids sealants, mastics, and coatings. Applications include specialty sealants, electrical potting and encapsulation compounds, and as a curable tackifier/plasticizer in blends with higher molecular weight polymers.

### Polyisobutylene

Polyisobutylenes (PIB) have the inertness of paraffinic hydrocarbons and cannot be cured or vulcanized using standard rubber technology. On a molecular weight basis they bracket the butyl polymers, are compatible with them, and can function in a manner similar to butyl in adhesive and sealant compositions that will not be cured. Contributions to finished composition performance are strongly influenced by PIB molecular weight.

The low molecular weight grades of polyisobutylene, Vistanex® LM-MS, LM-MH and LM-H, are permanently tacky, clear white to very light yellow semi-liquids, containing no stabilizer. They have broad acceptability in FDA regulated applications. These grades will show some degree of flow at elevated temperature and can be pumped and handled as liquids at temperatures of 150–180°C. Primary uses are as permanent tackifiers in a variety of cements, pressure sensitive adhesives, hot melt adhesives, and sealants. These polymers provide tack, softness, and flexibility and can assist in improving adhesion by "wetting out" various hard-to-adhere substrates. They are particularly useful for enhancing adhesion to polyolefin plastic surfaces. They can also serve as primary binders in soft, tacky, 100% solids sealant systems such as those used for insulated glass.<sup>5</sup>

The high molecular weight polyisobutylene grades, Vistanex MM L-80 through L-140, are white to light yellow, tough, rubberlike solids which contain less than 0.1% BHT stabilizer. These grades have a fairly wide acceptance in FDA regulated applications. They are used to impart strength and flow resistance to solvent cements, pressure sensitive adhesive label stock, and some sealants. They are also used in certain hot melt coatings and adhesives, where they provide improved flexibility and impact resistance, particularly at low temperatures.<sup>6</sup>

In addition to the Vistanex grades manufactured by Exxon Chemical Company a series of low and high molecular weight grades are available from BASF under the trade name Op-panol.

### Halogenated Butyl Rubber

*Chlorobutyl rubber*<sup>7</sup> is prepared by chlorinating the regular butyl polymer under controlled conditions so that reaction is primarily by substitution and little of the unsaturation originally present in the macromolecule is lost. The chlorine is believed to enter the molecule at the highly reactive allylic position, one carbon removed from a double bond. Approximately 1.2 wt % chlorine is present in the commercial grades of Exxon chlorobutyl. The chlorine

tends to enhance the reactivity of the double bonds as well as supply additional reactive sites for crosslinking. As a result, a wide variety of different cure systems can be used to vulcanize this elastomer.

Chlorobutyl can be readily blended and cured with other, more highly unsaturated elastomers. In the adhesives and sealants area, it has been blended with both regular butyl and natural rubber and then preferentially cured through the chlorine to improve strength. The reactive chlorine will also tend to increase adhesion to many polar substrates.

A *brominated butyl rubber* can be prepared in a manner similar to the chlorinated version. Bromobutyl is structurally similar to chlorobutyl but contains approximately 2.0 wt % bromine (in the case of the Exxon product) and provides an additional level of crosslinking activity.<sup>8</sup>

In addition to the grades of halogenated butyl rubber shown in the table, both brominated and chlorinated butyl polymers are produced by Polysar Limited, e.g., Polysar Chlorobutyl 1240.

### Butyl Rubber and Polyisobutylene Latices

Butyl rubber can be emulsified using anionic emulsifiers. A butyl latex might typically have a solids content of approximately 60 wt %, a pH of 5.5, a Brookfield viscosity of 2500 cps, and an average particle size of 0.3  $\mu\text{m}$ . BHT can be used as an antioxidant, with a small amount of preservative sometimes added.

Butyl latex has excellent mechanical, chemical, and freeze-thaw stability which allows for a wide latitude in compounding and blending with other ingredients. Because of its stability, it cannot be coagulated in a controlled manner using standard latex coagulants. When dried, it possesses the typical butyl characteristics of good aging, flexibility, low permeability, tack, etc.

Butyl latex can be used in packaging adhesive applications and as a tackifying and flexibilizing additive in higher strength adhesives based on more brittle polymers. It is noted for its compounded adhesion to polyolefin film and fibers, and is used in laminating and seaming

adhesives and specialty binders and coatings for both polyethylene and polypropylene.<sup>9</sup>

One supplier of butyl latex is Burke-Palmason Chemical Company (Pompano Beach, Florida). This company also manufactures polyisobutylene emulsions.<sup>10</sup>

### Modified Butyls

A number of partially crosslinked butyl rubbers and other modified forms of butyl are commercially available. Most of these are specifically produced for the adhesives and sealants markets.<sup>11</sup> Partially crosslinked butyls include Polysar's XL-20 and XL-50,<sup>12</sup> terpolymers in which DVB (divinylbenzene) is added during polymerization to impart a measure of cure. Hardman Inc. produces Kalar, a series of pelletized, partially crosslinked butyl products differing primarily in degree of crosslinking.<sup>13</sup> These products have added toughness, strength and flow resistance as a result of the crosslinks. The more tightly crosslinked grades are designed primarily for 100% solids butyl sealing tape and can serve as a base for butyl mastics. The more lightly crosslinked products are more appropriate for low shear, low horsepower equipment and where hydrocarbon solvent solubility is necessary, such as in solvent release caulks, pressure sensitive adhesives, and protective coatings.

Various depolymerized butyls, butyl rubber solutions or cutbacks, butyl/plasticizer blends, and highly plasticized/partially cured butyls are also available. These products are used by many adhesive companies where equipment limitations prohibit the use of the tougher, regular bale forms of butyl rubber. Principal suppliers of these type materials include Rubber Research Elastomerics, Inc., Minneapolis, Minnesota; ADCO Products, Inc., Michigan Center, Michigan; and A-Line Products, Detroit, Michigan.

## FORMULATING AND PROCESSING

### Choice of Polymer

The family of isobutylene polymers is extremely broad. This wide selection of completely compatible polymers permits the

knowledgeable compounder to achieve a wide range of properties. One example in adhesives and sealants formulating is the desire to increase cohesive strength while maintaining other valuable characteristics such as tack. There are a variety of ways in which cohesive strength can be modified by the proper polymer selection in polyisobutylene systems. The following techniques are presently of commercial interest:

1. For strength, choose the highest molecular weight polyisobutylene (PIB) or butyl rubber grade consistent with application or processing requirements.
2. Blend butyl rubber with polyisobutylene and cure the butyl portion. Since the PIB does not cure, the extent of the cure in the system and thus the cohesive strength is governed by the butyl content.
3. Partially cure butyl rubber. This can best be done by adding a carefully measured amount of curative and fully curing to the extent of the curative present, or by using one of the available precured grades.
4. Blend either PIB or butyl with halogenated butyl and cure only the halogenated butyl portion by utilizing the halogen functionality. As an example, a curative that will react with chlorobutyl and not with butyl is zinc oxide. This technique is also of interest in blends of halogenated butyl with either SBR or natural rubber for pressure sensitive adhesives.

Another example of the compounding latitude afforded by polymer selection in the polyisobutylene family is tack. Tack is increased with Vistanex LM low molecular weight PIB; butyl rubber can be depolymerized to any desired tacky state, or a wide range of compatible tackifiers can be incorporated.

In terms of the butyl polymers the variable of greatest interest to the adhesives compounder is usually molecular weight. All grades of butyl rubber are of such low unsaturation that this characteristic does not affect most performance properties in uncured or partially cured formulations. However, in applications not requiring cure the lowest unsaturation grades are usually chosen for optimum aging.

## Pigments and Fillers

The same pigments and fillers commonly used with other rubbers can be compounded with butyl rubber and polyisobutylene, and the general principles of selection are the same. Very fine pigments increase cohesive strength and stiffness, reduce cold flow, and also reduce tack. Platy pigments such as mica, graphite, and talc are preferred for acid and chemical resistance and low gas permeability. Some of the coarser pigments increase tack.

Zinc oxide increases tack and cohesive strength in these polymers (and also plays an important chemical role in the vulcanization of butyl). Aluminum hydrate, lithopone, whiting, and the coarser carbon blacks such as thermal blacks also increase tack with moderate increase in cohesivity. Clays, hydrated silicas, calcium silicates, silico-aluminates, and the fine furnace and thermal blacks increase cohesive strength and stiffness. Stiffness can also be increased by use of very fine silica pigment and magnesium oxide or carbonate.

Special situations call for specific types of pigments and fillers. Several examples illustrate this point:

1. Where cost is a prime consideration the calcium carbonates often produce adequate physical characteristics and are a good choice.
2. In the formulation of electrical tapes and mastics the fillers must be chosen for their electrical properties, both original and after water immersion. Mistron Vapor Talc and Satinton W/Whitetex clay are good selections.
3. If a degree of flame resistance or self-extinguishing property is required, the fillers must be chosen for this characteristic. In butyl the combination of antimony oxide and a halogenated flame retardant, usually used at about the 10/30–15/45 phr level, can impart substantial resistance to flame.
4. In compositions such as tacky, flow resistant sealing tapes (e.g., for automotive glazing), the filler must contribute to the strength of the product. In this case a

reinforcing black such as N330 (HAF) performs best.

Filler selection can be critical to the performance of the finished product and should be given careful consideration.

### **Tackifiers, Plasticizers, and Other Polymeric Additives**

As has been pointed out previously a wide range of properties, particularly rheological properties, can be obtained within the isobutylene family of polymers. In addition, a broad range of tackifiers and plasticizers can be used to extend the viscosity range and to control the tack and cohesive strength level. A common plasticizer is polybutene.<sup>14</sup> This material is available in a number of molecular weights so the viscosity and volatility can be selected for the application. Other liquid materials used as plasticizers include paraffinic oils, petrolatum, and certain phthalates with long, aliphatic side chains such as ditridecyl phthalate.

Resins are typically used in butyl and PIB-based adhesives and sealants to develop the desired level of tack. A wide range of resins can be used but the most common are probably the polyterpenes such as Piccolyte S115; the terpene-phenolics such as Schenectady's SP-553; phenol-formaldehyde resins such as Schenectady's SP-1068; the hydrocarbons like Escorez® 1102, Escorez 1304, and Escorez 1315, and modified rosins and rosin esters like Staybelite and Pentalyn. Usually these resins are used with plasticizers to obtain the desired balance of tack and cohesive strength.

Many other polymeric additives are used in butyl and PIB adhesives and sealants. Most worthy of mention are factice, which can lower cost, improve processing, and reduce stringing; amorphous polypropylene, which can reduce cost and improve processing as well as impart thermoplastic character; various waxes, which function in much the same manner as amorphous polypropylene; and asphalt, again for lower cost.<sup>15</sup>

Special materials used in butyl sealants or as primers to obtain bonds of PIB-based products to specific substrates such as glass are various organic silanes. An example is an epoxy silane

like A-187. There is evidence that amino silanes like A-1100 and methacryloxy silanes like A-174 may also be of value. In certain textile applications isocyanate primers or adhesion promoters can be used with butyl cements.

Antioxidants are often used in butyl and PIB adhesives and sealants to protect against severe environmental aging conditions such as ultraviolet light or heat. Materials such as Ethanox 702, Butyl Zimate, AgeRite White, Irganox 1010, BHT, and even sulfur have been used.

### **Curing Systems**

There are four curing systems of general interest in cements, adhesives, caulks, sealants, and coatings based on butyl and halogenated butyl.<sup>16</sup> These are (1) the quinoid cure, (2) cure with sulfur or sulfur donor compounds, (3) resin cure, and (4) for halogenated butyl only, the zinc oxide cure. The introduction of crosslinking increases cohesive strength and reduces cold flow as stated previously, but reduces tack and solubility in hydrocarbon solvents. Thus, crosslinking systems must be carefully designed for the specific application; they are used more in butyl based sealants than adhesives.

The quinoid cure is perhaps the most common. It is an old, easily controlled system that typically is formulated as a split batch, two-part cement designed to cure at or even below room temperature. The resultant network is tightly cured, highly resistant to ozone, heat, chemicals, and other environmental attack, and provides good electrical properties. Dark color bodies are formed during the reaction, so quinoid cures cannot be used to make white products, and even light colors require careful compounding. Differences in butyl polymer unsaturation have little effect on the speed of cure with quinoids.

Quinoid cures depend on crosslinking through the nitroso groups of aromatic nitroso compounds. A commonly used system employs *p*-quinone dioxime (commercially known as QDO) or dibenzoyl *p*-quinone dioxime (DBQDO), combined with an oxidizing agent such as manganese dioxide, lead dioxide, red lead oxide ( $Pb_3O_4$ ), or benzothiazyl disulfide. The DBQDO system is less active and thus is

easier to control at elevated temperatures. The actual crosslinking agent is believed to be the oxidation product, *p*-dinitroso benzene; dinitroso compounds introduced as such, for example *p*-dinitroso benzene on a clay base (Poly DNB), rather than formed by oxidation are also active crosslinking agents for butyl. An attraction of the quinoid cures to formulators is the aforementioned split batch nature, one part containing the dioxime, the other the oxidizer (usually either  $\text{MnO}_2$  or  $\text{PbO}_2$ ). The parts are combined just before use.

Sulfur curing systems for butyl include elemental sulfur, thiuram or dithiocarbamate accelerators and thiazole or thiazyl disulfide activators. Zinc oxide or other metallic oxides are necessary to attain satisfactory cure. The relatively minor differences in unsaturation between grades of butyl are significant with sulfur cures, the rate of cure and number of attainable crosslinks increasing with increasing polymer unsaturation, while chemical and ozone resistance decrease. The need for elevated temperature to attain crosslinking limits utility of sulfur cures in adhesives and sealants applications.

The resin cure of butyl normally uses one of a series of active, brominated phenolic resins such as Schenectady's SP-1055. The resin cure of butyl can proceed at temperatures from ambient to very high depending on the specific resin chosen and on the concentration and type of cure activator. Features of the resin cure are high stability, heat resistance, and the capability to be compounded into light colored and white formulations.

The zinc oxide cure of chlorobutyl and bromobutyl is of interest in sealants and adhesives primarily because it allows these polymers to be cured in the presence of other elastomers without affecting the other elastomers. The zinc oxide cure is also of interest in certain FDA sensitive applications where the elegant simplicity of a compound that contains only a polymer and zinc oxide has obvious appeal.

If it is desired to cure only a small fraction of the polymer base, this can be done in two ways. A small and carefully measured amount of curative can be used and reacted to the full extent of the curative present to produce a par-

tial cure. Alternatively, a portion of chlorobutyl or bromobutyl can be blended with a polymer which does not cure via zinc oxide, for example butyl, an excess of zinc oxide can be added and the dispersed halogenated butyl phase totally cured. The result of this "preferential" cure technique is butyl with higher cohesive strength for use as a sealant or adhesive base.<sup>17</sup> Similarly, halogenated butyl can be blended with natural rubber and then the halogenated butyl phase cured with zinc oxide. The resultant material is a high cohesive strength base for pressure sensitive adhesives.

### Solvents and Solution Processing

Butyl rubber and polyisobutylene polymers are soluble in hydrocarbon and chlorinated solvents, but not in the common alcohols, esters, ketones, and other low molecular weight oxygenated solvents. Volatile paraffinic solvents such as hexane, heptane, and naphtha are often used in cement and adhesive work. Cyclohexane and the chlorinated solvents like perchloroethylene give solutions of much higher viscosity on an equal weight percentage basis than the common paraffinic and aromatic solvents. A substantial part of this difference is due to the much higher specific gravity of chlorinated solvents. The low solubility in oxygenated solvents is often useful since butyl and PIB films can withstand immersion in these common solvents.

An important consideration in solvent selection is air pollution requirements. For this reason solvents such as Laktane (quite fast), VM&P Naphtha (medium evaporation rate), and mineral spirits (slow) are generally of interest. The latter two can be purchased to comply with regulations such as Southern California Air Pollution Control District Rule 102 (formerly Rule 66).

The presence of minor amounts of stabilizer and metal stearate in butyl and PIB may cause pure gum cements to be slightly cloudy even though the polymer is completely dissolved. Under certain circumstances, these materials will slowly settle out of low viscosity solutions of the polymers. The only deficiency is in appearance, and the settling can be avoided or re-



tarded by working with higher viscosity solutions.

The relationship between solids and viscosity for various butyl and PIB polymers is logarithmic as is shown in Figs. 2 and 3.<sup>18</sup> A small change in solids can make a large difference in solution viscosity, especially at higher solids levels. Viscosity is also strongly dependent on polymer molecular weight and a small change in the molecular weight of the polymer can result in a relatively large change in the viscosity of polymer solutions.<sup>19</sup>

The optimum solids level of cements to be applied by various methods is, of course, subject to broad variation depending on the solvent selected (i.e., the viscosity which results), filler content, etc. In general, butyl rubber and polyisobutylene cements for application by spraying contain 5–10% solids, for dipping 10–30%, for spreading 25–55%, and for application by finger or spatula, 50–70%.

Due to the low permeability of butyl and PIB polymers, gum cements should be applied in thin coats to facilitate solvent release and avoid porosity. Adequate drying time should be permitted between coats when multiple applications are needed to increase thickness. Cements containing appreciable volumes of filler are less sensitive in this respect.

The various butyl and high molecular weight PIB grades (e.g., Vistanex MM) are marketed

in solid, bale form. To facilitate solvation for adhesives and mastics use, a common initial step is to increase surface area greatly by physical size reduction and thereby decrease solvation time. This can be accomplished using a (1) bale chopper or granulator, (2) sheet mill and slab chopper, or (3) Banbury, sheet mill, and slab chopper. It is important that the shredded polymer be stored for only a short time since it will reagglomerate.

The output of the shredder is most efficiently utilized by directing it into the subsequent solvation equipment. One clever and quite inexpensive unit uses a modified meat grinder mounted on the solvation tank to feed polymer particles from the grinder directly into agitated solvent.

Butyl polymers do not require the work input of a mill or Banbury to be solvated; simple chopping is quite adequate. Mills and Banburys, if available, can be used to incorporate other materials such as fillers into the polymer before solvation.

Low molecular weight polyisobutylene (e.g., Vistanex LM) and low molecular weight butyl, with their semi-liquid forms, are much more rapidly solvated than the higher molecular weight analogs. It is advantageous to permit these low molecular weight polymers to flow gradually from their container directly into agitated solvent.<sup>20</sup> Fillers and other compounding

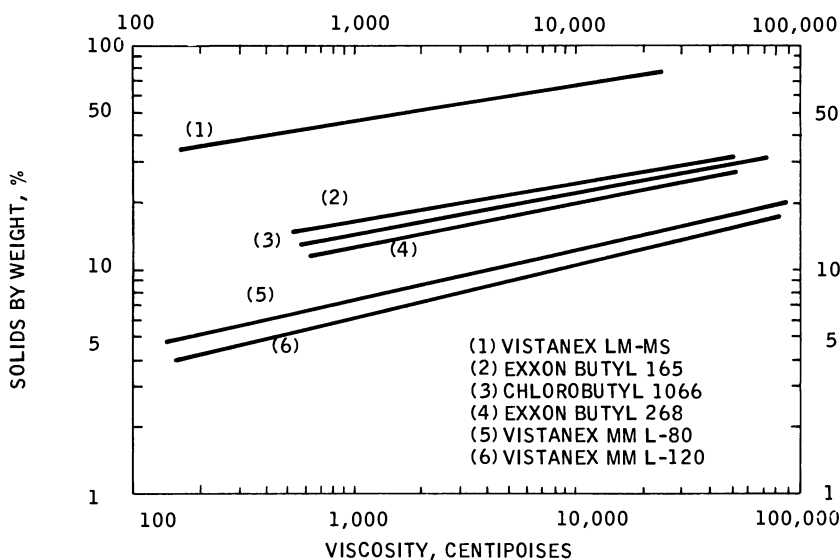


Fig. 2. Solution viscosities of isobutylene elastomers in toluene.



is involved. By way of example the preparation of butyl caulks and mastics can follow several routes. The most common are as follows:

1. A heavy duty kneader is used to make a butyl rubber solution, normally in mineral spirits. The solution is made by charging the rubber into the kneader and working the solvent slowly into the rubber. The solvent must be added particularly slowly at first, and each increment of solvent must be incorporated into the batch before more is added. If solvent is added too rapidly, the polymer will be dispersed in the form of small pellets and these pellets can only be dissolved by extended subsequent mixing. Adding solvent too fast results in either greatly increased batch cycle time to obtain uniformity or in polymer particles in the final solution. Normally the finished solution is transferred into another less expensive, lower powered mixer for further compounding, e.g., the addition of the pigments, resins, plasticizers and other ingredients.

2. In a heavy duty kneader the butyl is mixed with all the nonvolatile ingredients and then solvated. The same precautions apply to the mixing and solvation steps as were outlined above; that is, each increment must be well dispersed before subsequent additions are made. There are two different orders of addition used in this technique:

- a. Normally the rubber is added first to the kneader and the dry ingredients are then slowly incorporated.
- b. Alternatively, the "upside down" technique has been found to result in better dispersion in less time, especially in the case of mastics based on partially cross-linked butyl. In this technique the fillers and a small amount of plasticizer are blended into a smooth, stiff paste in the kneader and the rubber is added last.

3. A masterbatch of polymer and filler can be prepared on a mill or in a Banbury and this masterbatch is then solvated in another mixer. For very high viscosity mixtures (essentially like conventional rubber compounds), such as blends of rubber with filler (and/or plasticizers), mills and Banburys are the best choice.

The general outline of butyl caulk preparation is shown in Fig. 4.

The production of sealing tapes generally follows similar procedures but solvents are not used. One piece of equipment that should be highlighted for tape production is the screw discharge kneader.<sup>21</sup> This kneader type is particularly efficient for tape production where it allows short total cycles. The tape compound can be mixed and quickly extruded either in finished form or in slug preforms which are easy to use in subsequent extrusion operations.

Since a great deal of butyl and polyisobutylene is used to modify wax, and since the technique to make wax blends is quite sensitive, it deserves special mention. If PIB is used, it is placed in a kneader and allowed to work until it attains a maximum surface area. This is often termed *ricing*, since PIB at this stage looks like cooked rice. The wax is slowly added to this riced rubber. It is especially important that the quantities of wax added, especially initially, be quite small and that the mix be allowed to become homogeneous before more wax is added. Butyl rubber will tend to *band* rather than *rice* in a kneader, but the same slow initial wax addition procedure must be followed.

## APPLICATIONS AND FORMULATIONS

The inherent properties of polymers of the polyisobutylene family, particularly the chemical inertness, age and heat resistance, long-lasting tack, flexibility at low temperatures, and the favorable FDA position on selected grades, make these products commercially attractive in a variety of pressure-sensitive and other adhesives, in automotive and architectural sealants, and in coatings. An added dimension is achieved in the blendability of the polyisobutylene polymers with each other and with other adhesive polymers such as natural rubber, styrene-butadiene rubber, EVA, low molecular weight polyethylene, and amorphous polypropylene to achieve specific properties. They can, for example, be blended with the highly unsaturated elastomers to enhance age and chemical resistance. A description of polyisobutylene polymer family use in adhesive and sealant applications follows.

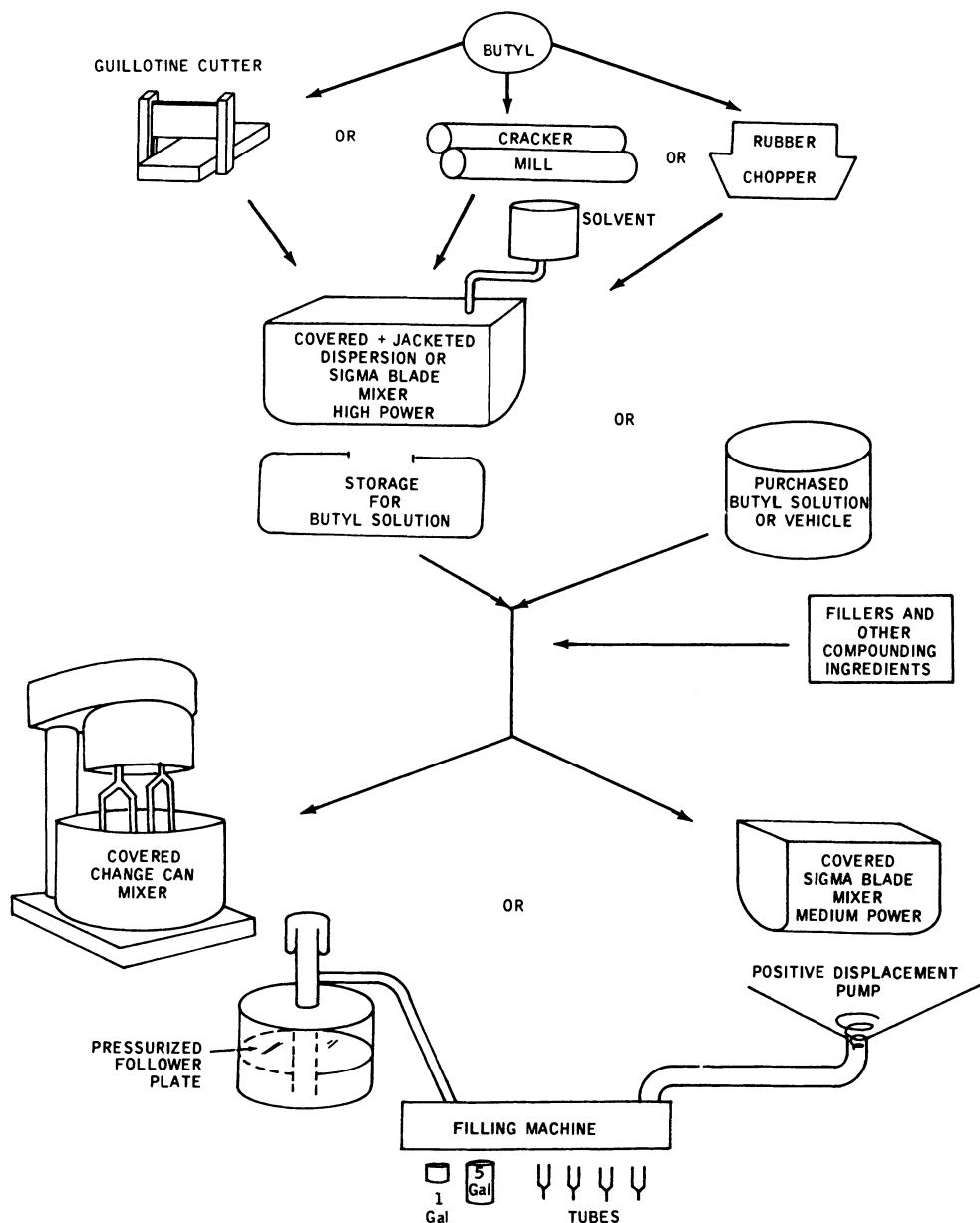


Fig. 4. Typical flow plan for butyl caulk manufacture.

## Adhesives and Mastics

**Miscellaneous Cements.** Butyl and polyisobutylene are used in a range of cements. Several specific types shown in Table 2 illustrate their use. All concentrations in formulations in this chapter are expressed in parts by weight.

Two-part, self curing cements based on butyl

are well known and are used in a variety of applications where the properties of the butyl polymer are desired. Two typical starting point formulations are shown in Table 3.

**Pressure Sensitive Adhesives.**<sup>22</sup> Solution pressure sensitive adhesives (PSA's) for tapes and labels are primarily blends of rubber and tackifying materials such as resins. The low

**Table 2. Miscellaneous Cements.****a. Paper Cement**

Vistanex MM L-100	100
Solvent	900

This cement is similar to that sold for home and office use.

**b. Laminating Cement For Polyethylene Film**

Exxon Butyl 268	100
Terpene phenolic resin <sup>a</sup>	5
Solvent	to appropriate viscosity

This cement is solvent coated on one substrate and dried. The second substrate is then laminated to the adhesive with moderate roll pressure. In this way the natural tack of the formulation allows impervious material to be laminated without solvent entrapment.

**c. Flocking Adhesive**

Vistanex MM L-100	100
Terpene phenolic resin <sup>a</sup>	20
Butyl Zimate	0.5
Solvent	to appropriate viscosity

<sup>a</sup>Schenectady SP-553 or similar resin.

molecular weight polyisobutylenes find use as permanent tackifiers and modifiers. They enhance tack and softness and can contribute to adhesion by improving wetting of the substrate. The higher molecular weight products serve as the rubbery base materials.

Two important parameters in the formulation of pressure sensitive adhesives are *tack* and *hold*, which is the ability to resist creep under deadload. As noted, butyl and polyisobutylene are inherently tacky polymers. This tack can be enhanced with a wide variety of resins and other tackifiers. The hold or cohesive strength is low compared to some other pressure sensitive adhesive polymers, such as natural rubber, but can be increased if required by (1) incorporation of high molecular weight PIB or natural rubber, (2) the choice of the other ingredients, particularly resins and fillers, and (3) the partial or preferential curing techniques noted previously. The polyisobutylene polymers are primarily used in label pressure sensitive adhesives and in certain tapes where high cohesive strength is not necessary.

The age resistance of polyisobutylene polymers manifests itself as a lack of hardening and

**Table 3. Butyl Based Curing Cements.****a. Butyl Self Curing Cement**

	Part A	Part B
Exxon Butyl 268	50	50
Zinc oxide	2.5	2.5
Stearic acid	1.5	1.5
N762 (SRF) carbon black	—	40
Staybelite Ester 10 resin	20	—
Sulfur	0.7	0.7
QDO	2	—
Lead dioxide	—	4
Solvent: heptane	400	400
92% isopropanol (wet)	5	5

The dry ingredients are milled into the rubber and the resultant blend is dissolved as indicated. The two parts are mixed just before use.

**b. Chlorobutyl High Strength Cement**

Chlorobutyl 1066	100
Ditridecyl phthalate (DTDP)	5
Diethyl thiourea (DETU)	5
Toluene	360
Isopropyl alcohol	40

**Procedure**

1. Preblend a paste of DETU in warm DTDP.
2. Banbury or mill mix the compound for 5 min at 240 to 280°F.
3. The temperature *must* be kept below 300°F.
4. Solvate the base stock.

High shear mixing at moderate temperature will result in the formation of a thiouronium salt which through ionic bonding will increase the green strength of the gum polymer while still maintaining full solubility. This base is a good high strength cement in its own right. To obtain a room temperature curing cement, add just before use:

Zirex (Zinc resinate)	10
Toluene	10

permanency of tack, and this has led to their use where long service life or aged adhesive integrity is required as, for example, in removable label pressure sensitive adhesives. A removable label adhesive which ages poorly may lose cohesive strength and consequently will not peel as cleanly as desired. The higher molecular weight grades when used as the base polymer also die cut well, an important requirement for use in labels. Butyl and polyisobutylene are thus preferred materials in

removable pressure sensitive label and protective tape adhesives.

The low temperature flexibility and tack of these polymers results in a service temperature range extending below ambient. Vistanex LM low molecular weight PIB is a particularly useful low temperature tackifier. The polyisobutylene polymers find application in solvent-borne, low temperature pressure sensitive adhesives such as freezer label adhesives.

The low order of toxicity, favorable FDA status, and light color result in a variety of medical pressure sensitive adhesive uses for selected polyisobutylene polymer grades. Applications include surgical tape, oral bandages and ostomy appliances.

Adhesives formulated with butyl and polyisobutylene are used for adhesion to a variety of substrates including nonporous, hard-to-adhere-to materials such as polyethylene. Other common substrates include paper, polyvinyl chloride, and polyester film.

Several typical or starting point solution pressure sensitive adhesive formulations illustrating some of the uses described above are given in Table 4. They are provided for general guidance on materials selection and quantity but likely require modification to suit specific ingredients, manufacturing, and finished property requirements.

**Hot Melt Adhesives.** The isobutylene family of polymers can also be formulated in hot melt compositions, both pressure sensitive and non-pressure sensitive, and can impart many of the same property benefits noted for solvent based systems. These polymers improve flexibility, particularly at low temperatures, provide good aging and chemical resistance, and serve to contribute toughness and strength in thermoplastic mixtures. Increases in hot tack, adhesion and overall seal strength have been widely documented.<sup>23-27</sup> Polyisobutylene grade choice and concentration are important considerations, however, in that these elastomeric products become more difficult to melt mix, significantly increasing melt viscosity as PIB molecular weight increases. High molecular weight grades (e.g., Vistanex MM), in fact, are limited in hot melt applications.

**Table 4. Pressure Sensitive Adhesives.**

a. Simple PSA for Transparent Tape

Exxon Butyl 268 or Vistanex MM L-100	100
Vistanex LM-MS	75
Solvent	to coatable viscosity

b. Chlorobutyl Blend PSA for General Purpose Tape

Chlorobutyl 1066	50
SBR 1011	50
Vistanex LM-MS	30
Escorez® 2393 resin	30
Pentalyn H resin	30
Antioxidant <sup>a</sup>	0.5
Solvent	to coatable viscosity

c. Removable Label Stock PSA

Vistanex MM L-100	100
Vistanex LM-MS	40
Zinc oxide	20
Calcium carbonate	20
Escorez 5300 resin	30
Polyterpene resin (115°C S.P.) <sup>b</sup>	30
Polybutene (avg. MW 1300) <sup>c</sup>	45
Paraffinic process oil	15
Antioxidant	0.5
Solvent	to coatable viscosity

d. Vinyl Floor Tile PSA

Exxon Butyl 268	100
Vistanex LM-MS	20
Terpene phenolic resin <sup>d</sup>	70
Solvent	to coatable viscosity

e. Solvent Adhesive for Surgical Tape

Vistanex MM L-100 <sup>e</sup>	100
Vistanex LM-MS	30
Zinc oxide	50
Hydrated alumina	50
USP white oil	40
Phenol formaldehyde resin <sup>f</sup>	50
Solvent	to coatable viscosity

<sup>a</sup>e.g., Irganox 1010 or Ethanox 702; these products can be used in all recipes where antioxidant is indicated.

<sup>b</sup>Piccolyte S115 or equivalent resin.

<sup>c</sup>e.g., Parapol® 1300.

<sup>d</sup>Schenectady SP-553 or similar resin.

<sup>e</sup>A minor percentage of the Vistanex MM L-100 can be replaced by natural rubber if increased cohesive strength is desired. In this case, an antioxidant may be required for age stability.

<sup>f</sup>Schenectady SP-1068. Aliphatic hydrocarbon resins such as Escorez 1304 can also be used.

For hot melt pressure sensitive adhesives<sup>28</sup> butyl rubber is usually blended with significant amounts of melt materials, e.g., tackifying

resin, petrolatum, and amorphous polypropylene, to reduce viscosity to desirable levels. Low volatility hydrocarbon oils, polybutenes and paraffin, and microcrystalline waxes also depress melt viscosity, but excessive wax can adversely affect tack. Low molecular weight PIB is an effective butyl plasticizer and enhances tack. Applications for butyl hot melt pressure sensitive adhesives often involve long service life, low temperature, and polyolefin plastic film adhesion, capitalizing on the inherent features of the polymer noted previously. An illustrative starting point formulation for adhesive-backed carpet tiles is shown in Table 5.

The low molecular weight PIB grades are perhaps the most functional polyisobutylene polymers for hot melt pressure sensitive adhesives. They are easiest to melt mix and result in low viscosity blends due to their low molecular weight. Brookfield viscosity at 177°C (spindle SC4-27) is typically 30,000–60,000 cps depending on grade, and melt viscosity can readily be tailored to meet specific requirements by incorporation of thermoplastic ingredients.<sup>15</sup>

Petrolatum and waxes are most effective as viscosity depressants. Resins, waxes, and thermoplastics such as low density polyethylene (LDPE), ethylene vinyl acetate, and crystalline and amorphous polypropylene increase hardness and cohesive strength. LDPE and crystalline polypropylene particularly raise blend softening point, even at the 10 wt% concentra-

tion level, thus extending adhesive service temperature range. Waxes and thermoplastics must be used in moderation, however, since they reduce the tack of the finished blend. Hydrocarbon oils and petrolatum plasticize and bring out aggressive tack in low molecular weight PIB, resin mixtures.

Blends containing low molecular weight PIB can be prepared with relative ease. Added incrementally, it dissolves quite effectively in the liquid and molten melt ingredients of an adhesive composition at 180°C with agitation.

Several formulations illustrating low molecular weight PIB use in hot melt pressure sensitive adhesives are provided in Table 6.<sup>15,29</sup> This polymer functions as an age resistant tackifier, adhesion promoter and flexibilizer, and its favorable FDA regulatory position extends use to medical applications. Again, these formulations should be considered as starting points only.

In non-pressure sensitive compositions all of the above formulating approaches are applicable but now one need not be concerned with room temperature tack, i.e., pressure sensitivity.

Again low molecular weight PIB is used as a tackifier and adhesion promoter,<sup>27</sup> particularly in packaging applications where adhesion to polyethylene and other plastic film surfaces is desired. A general formulation illustrating use in packaging adhesives is shown in Table 7.

Butyl rubber is used in preformed, hot melt adhesive rods which can be fed through various types of automatic dispensing equipment. Butyl provides both strength and flexibility to the adhesive "rope" before application, flow control during application, and improves the properties of the adhesive bond.<sup>30,31</sup> A formulation for a typical rope or coil form of hot melt adhesive is shown in Table 8.

**Table 5. Butyl Rubber Hot Melt Pressure Sensitive Adhesive**

Exxon Butyl 065	100
Escorez 1304 resin	100
Petrolatum (57°C M.P.)	50
Amber microwax <sup>a</sup>	150
Antioxidant	1
Brookfield viscosity at 121°C	
Spindle SC4-29 (cps)	80,000
Surface	Tacky, firm
Adhesion <sup>b</sup>	
Vinyl foam to plywood	Good–excellent
Rubber foam to plywood	Good–excellent

<sup>a</sup>Be Square 175.

<sup>b</sup>Adhesives coated on foam and subsequently manually pressed onto plywood.

**Wax Blends.** A related application for the isobutylene polymers is as a specialty additive in wax compositions. They serve to impart increased viscosity, added toughness and strength, improved seal strength and adhesion, improved flexibility particularly at low temperatures, and also add a degree of aging and chemical resistance.<sup>32</sup> In coatings low levels

**Table 6. Low Molecular Weight Polyisobutylene Hot Melt Pressure Sensitive Adhesives.**

A. General Recipes			
	1	2	3
Vistanex LM-MS	25	35	45
Escorez 1310 resin	50	50	15
Petrolatum (57° C M.P.)	15	—	40
High MW LDPE <sup>a</sup>	10	—	—
Paraffinic process oil	—	15	—
Brookfield viscosity at 177°C spindle SC4-27 (cps)	1900	1200	850
Surface	tacky, firm	very tacky, soft	very tacky, soft
Softening point, ring and ball (°C)	101	49	55
B. Low Temperature Label Pressure Sensitive Adhesive			
Kraton 1107 <sup>b</sup>		50	
Finaprene 1205 <sup>b</sup>		50	
Vistanex LM-MS		90	
Escorez 2393 resin		130	
Naphthenic process oil		58	
Antioxidant		2	
Rolling ball tack (cm)		2.5	
180° Peel (g/cm)			
Stainless steel		880	
Treated LDPE		570	
180° Peel at 0°F (g/cm) <sup>c</sup>			
Stainless steel		1250	
Treated LDPE		90	
Loop tack at 0°F (g/cm) <sup>c</sup>			
Stainless steel		950	
Corrugated board		290	
Waxed board		410	
C. EVA Based Pressure Sensitive Adhesive			
Elvax 40		100	
Vistanex LM-MS		20	
Escorez 2393 resin		80	
Antioxidant		1	

<sup>a</sup>A low MW LDPE grade such as Epolene C-10 would give lower viscosity and softening point.<sup>b</sup>Styrene block copolymers.<sup>c</sup>Adhesive and adherend conditioned at -18°C before contact; adhesion determined at -18°C.**Table 7. Hot Melt Packaging Adhesive.**

Ethylene vinyl acetate copolymer	25
Microcrystalline wax	30
Escorez 2393 resin	35
Vistanex LM-MS	10
Antioxidant	0.5

(1–5%) of butyl or high molecular weight PIB serve to promote holdout properties of many formulated waxes by increasing viscosity. High molecular weight PIB is used as a component in coating for cheese wrap where it imparts flexibility and resistance to natural oils and fats.



**Table 8. Rope Form of Hot Melt Adhesive.**

Exxon Butyl 268	20
Beta-Pinene Resin (115°C S.P.)	20
Escorene® UL 7750 EVA polymer	20
Low MW polyethylene (12,000 MW)	20
Low MW polyethylene (20,000 MW)	19
Antioxidant	1

**Pipe Wrap and Electrical Tapes.** The polyisobutylene polymers have a history of excellent performance in pipe wrap tape and in a variety of electrical tape areas. These applications exploit the age resistance, low water absorptivity and permeability, inherent tack, and electrical insulative properties of these polymers.

Pipe wrap tape is most commonly an adhesive based on butyl rubber or possibly a blend of butyl and ethylene propylene rubber<sup>33</sup> on a polyethylene or polyvinyl chloride backing. A formula for the adhesive is shown in Table 9. High molecular weight grade, Exxon Butyl 268, is used for maximum cohesive strength at high loading levels. Low unsaturation grade, Exxon Butyl 065, can be used if maximum age resistance is desired. Resins are chosen for tack and cohesive strength balance, and high resin levels combined with polybutene provide a tacky, pressure sensitive adhesive type pipe wrap tape. These adhesives are either calendared onto the backing, extruded, or solvated and coated from solution.

Electrical tapes based on butyl are actually bulk mastics compounded for good electrical, heat, aging, and ozone resistant characteristics.<sup>34</sup> Tapes for splicing and terminating wires and cables are self-fusing (i.e., when wrapped upon itself the tape must fuse, forming a per-

manent bond). Additionally, PIB tapes, particularly those tackified with low molecular weight PIB, provide good adhesion to polyethylene and thus are often the products of choice for splicing crosslinked polyethylene insulated cables. Splicing tapes are unsupported (as used they do not have a fabric or film backing) and are typically available in roll form on a release liner.

There are numerous pressure sensitive tapes with various adhesive and backing combinations for specific electrical applications. The nonpolarity of the polyisobutylene polymers makes them quite resistant to attack and swelling by the commonly used vinyl plasticizers. Thus, they are less susceptible to softening when used on vinyl film backings.

Typical nonconductive splicing tape and pressure sensitive electrical tape formulations are given in Table 10. The splicing tape mix is subjected to brief heat treatment in a Banbury

**Table 10. Electrical Tape Formulations.****a. Butyl Nonconductive Splicing Tape**

Exxon Butyl 268	100
Vistanex MM L-100	10
AgeRite Resin D	1
Zinc oxide	5
Mistron Vapor Talc	60
Satinton W/Whitetex clay	60
N990 (MT) carbon black	10
Low density polyethylene	5
Escorez 1315 resin	5
Alkyl-phenol resin <sup>a</sup>	5
Poly DNB	0.5
QDO	0.2

Tensile strength (psi)	650
Ultimate elongation (%)	750
Dielectric strength (volts/mil)	745
Volume resistivity (ohm-cm $\times 10^{-14}$ )	140

This compound is prepared in a Banbury mixer and held for about three minutes at 163°C to allow the promoters (Poly DNB and QDO) to couple the polymer and fillers. All properties measured on 0.030 inch thick uncured pads.

**b. PSA for Plastic Film Backed Electrical Tape**

Vistanex MM L-100	100
Escorez 2393 resin	35
Hercolyn D resin	35
Polybutene (avg. MW 950) <sup>b</sup>	35

**Table 9. Butyl Mastic for Pipe Wrap Tape.**

Exxon Butyl 065	100
N550 (FEF) carbon black	100
Mistron Vapor Talc	200
Polybutene (avg. MW 950) <sup>a</sup>	100
Escorez 1304 resin	75
Amorphous polypropylene <sup>b</sup>	50
Paraffinic process oil	50

<sup>a</sup>e.g., Parapol 950

<sup>b</sup>A-Fax 600 or similar product

<sup>a</sup>e.g., Schenectady SP-1077.

<sup>b</sup>e.g., Parapol 950.

mixer to maximize cohesive strength and electrical properties.

### Sealants

Butyl rubber and sometimes certain polyisobutylene grades are used as the base or binder in a wide range of commercially available caulking and sealing compounds. The major advantages noted for butyl based sealants in field performance are their permanent flexibility, elongation, outstanding age and weather resistance, and resistance to hardening.<sup>35,36</sup>

Caulks and sealants made from the isobutylene polymer family are available in three forms. As bulk sealant materials, they are usually one-part, plasticized systems, compounded with suitable inert fillers and solvents and designed for application with a standard caulking gun. As preformed tapes or *ribbon sealers*, they are 100% solids, tacky materials, supplied in roll form on a release paper backing and designed for easy hand application in areas which usually require compressive confinement for an effective seal. Finally, in a newer format as 100% solids, hot melt compositions, they are specif-

ically designed to be applied at elevated temperature by pressurized hot melt applicators directly to the substrates to be sealed.

### Solvent Release Sealing Compounds.<sup>37</sup>

The low unsaturated butyl grades (e.g., Exxon Butyl 065) are most commonly used in sealing compounds. The butyl polymer is usually prepared or purchased as a high solids cutback in mineral spirits. The solvent serves to plasticize the tough rubber, and when the finished sealant is put in place solvent evaporation causes the caulk to set and develop its properties. Other ingredients include a combination of extender pigments such as talc, whiting, and titanium dioxide, tackifiers and plasticizers such as resins and polybutenes, and, many times, low molecular weight polyisobutylene (e.g., Vistanex LM-MS) and other specialty additives. A typical butyl caulk formulation is shown in Table 11.

Butyl caulking compounds are used for general purpose construction sealing, for the bedding of glass, sealing various lap joints and some butt joints, in channel glazing, for do-it-

**Table 11. Butyl Rubber Based Caulking Compound.**

<i>Formulation</i>	<i>Parts by Weight</i>	<i>Wt %</i>
Exxon Butyl 065, 50% in mineral spirits	200	20.50
Vistanex LM-MS	20	2.05
Isostearic acid	5	0.51
Fibrous talc	300	30.75
Atomite whiting	200	20.50
Rutile titanium dioxide	25	2.56
Schenectady SP-553 resin	35	3.60
Parapol 1300 polybutene	100	10.25
Blown soya oil, Z <sub>3</sub>	15	1.54
Cobalt naphthenate drier, 6%	0.5	0.05
Cab-O-Sil M5	20	2.05
Mineral spirits	55	5.64
	975.5	100.00
Solids, wt %	84	
Density	1.37	
Pounds per gallon	11.4	

### Mixing

This batch was mixed in the order listed above in a sigma bladed kneader. The hard resin was predispersed in solvent for easier addition. Some slight formulation changes may be required to accommodate individual needs and equipment. In particular, mix times and shear rates can vary widely and slight variations in solvent content/thixotrope level may be needed to compensate for mixing differences.

yourself home repair, and in various industrial, interior duct and panel sealing, and marine applications. The excellent aging and ability to withstand some degree of movement are major advantages for butyl sealants over the traditional oil-based caulking compounds. High quality butyl caulking compounds will meet the requirements in Federal Specification TT-S-001657, "Sealing Compound-Single Component, Butyl Rubber Based, Solvent Release Type." Canadian Government Specification 19-GP-14 also covers Butyl Caulking Compounds.<sup>38</sup>

A different type of butyl mastic with a much lower viscosity is used by the canning and closure industry where highly automated application equipment applies a thin bead of sealant on metal can ends. Here the good FDA regulatory status and chemical resistance of butyl are valued.

**Sealing Tapes.**<sup>39</sup> The 100% solids, preformed tape sealants, because of their form and ease of handling, provide economies in installation often unattainable with other sealants. Tape rolls are available in a variety of widths and thickness and many times contain an embedded string or cured rubber core to prevent stretching or *drawdown* in use. All tapes have some degree of pressure sensitivity and are sufficiently soft to allow for ease of compression during installation.

Tapes can be categorized as nonresilient, semi-resilient, or resilient depending on their elastic properties. The nonresilient tapes or rope caulks are extremely soft materials which are usually based on polybutenes. Small amounts of low molecular weight PIB or butyl rubber are often added to improve strength and flow resistance. They are used in noncritical sealing and glazing applications where little movement is expected, e.g., in appliance sealing and in sealing trailer bodies and mobile homes.

The semi-resilient tapes are more elastic in nature and are usually based on regular butyl rubber. Both reinforcing and extender pigments are used to maintain a balance between compressibility and elasticity. The higher molecular weight polybutenes are used as plasticizers and tackifiers because of their better aging properties. A typical formulation for semi-re-

**Table 12. Semi-resilient, Butyl Based Sealing Tape.**

Exxon Butyl 268	100
Silene 732D silica	50
Titanium dioxide	50
Atomite whiting	300
Mistron Vapor Talc	150
Parapol 1300 polybutene	200
AgeRite White antioxidant	2

silient sealing tape is shown in Table 12. Semi-resilient tapes are used in a number of applications in curtain-wall and prefabricated constructions. They are often used as part of a systems approach to glazing and sealing where they are used in conjunction with other types of gunnable and/or chemically curing sealants.

The highly extensible, resilient tapes are based on partially/preferentially cured butyl or chlorobutyl rubber with pigments and plasticizers added to maintain a balance of properties. Once installed, these tapes exhibit excellent recovery from extension and compression so that an effective seal will be maintained despite wide latitudes of movement.

Resilient tapes are also used in the automotive area for the sealing of windshields and backlites. These tapes not only seal but also serve as the primary adhesive to hold the window glass in place. Although OEM use has declined in recent years, tapes are still used extensively in the aftermarket. Partially cured butyl is used exclusively in these tapes in order to meet the requirements of high shear strength, absence of flow and sag, and the ability to withstand the varied exposure conditions and vibrations encountered in a moving automobile.

Two resilient tape formulations illustrating the use of both commercially available precured butyl and butyl cured during mixing are shown in Table 13.

Fig. 5 illustrates two window seals made with butyl based sealing tapes. Fig. 5A shows tapes used to seal both the outside and inside of a window. Having an initial thickness slightly greater than the width of the channel for the seal, the tape is compressed and held firmly against the glass by the interior sash. Fig. 5B shows the tape being used to seal the outside of

**Table 13. Resilient Sealing Tapes.**

A.		B.	
Partially crosslinked butyl rubber	100	Exxon Butyl 065	60
Silene 732D silica	50	Chlorobutyl 1066	40
N326 (HAF-LS) carbon black	140	Coated calcium carbonate	50
Parapol 950 polybutene	140	N326 (HAF-LS) carbon black	100
Hercolyn resin	30	Parapol 950 polybutene	115
		Zinc oxide	2
		Magnesium oxide	0.4
		Stearic acid	0.4
One step kneader mix		Two stage mix:	
		<ul style="list-style-type: none"> <li>• Banbury masterbatch: butyl, Chlorobutyl, <math>\text{CaCO}_3</math>, <math>\text{ZnO}</math>, <math>\text{MgO}</math>, stearic acid; mix 5 min at 325°F</li> <li>• Kneader mix: masterbatch plus other ingredients.</li> </ul>	

a window while a gunnable caulk is employed on the inside.

**Insulated Window Sealants.**<sup>40</sup> Sealants used in the construction of double pane, insulated window and door units must not only possess excellent weathering, aging, and durability characteristics but must also have a low moisture vapor transmission rate and be nonfogging. The butyl polymers fulfill all of these requirements and have been successfully used in insulated glass sealants for many years.

A typical construction involves a combination system employing a butyl mastic as the barrier sealant between the metal spacer and glass and a back-up, chemically curing sealant serving as an adhesive to hold the unit together. An insulated glass mastic formulation is shown in Table 14. Vistanex LM low molecular weight PIB is combined with a platy talc filler

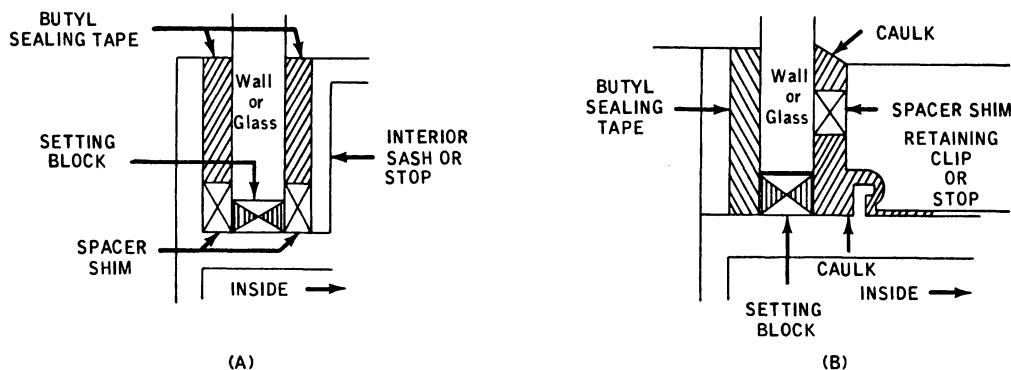
**Table 14. Insulated Glass Extruded Mastic.**

Vistanex LM-MH	100
Mistron Vapor Talc	48
N990 (MT) carbon black	2

which further enhances the moisture barrier properties of the system. Insulated glass sealants based on Vistanex LM are noteworthy for their outstanding performance after more than 20 years of field service.<sup>41</sup>

Other insulated glass sealants are designed as hot melt compounds with regular or partially cured butyl as the base. These compounds are either hot pumped into place or are applied in a thermoplastic, preformed tape construction.

**Hot Melt Sealants.** As mentioned above, a newer approach to applying sealants involves

**Fig. 5. Typical architectural tape installations.**

the use of 100% solids, thermoplastic compounds which are heated to lower their viscosity and then applied as hot melts. These products are also known as hot flow sealants. Butyl rubber serves as the elastomeric binder with amorphous polypropylene and various resins being used to impart thermoplastic properties.<sup>42</sup> Blends of butyl and ethylene propylene rubber and precured butyl can also be used, but in all cases formulations must be carefully tailored to avoid excessive melt viscosity. Polymers such as LDPE and EVA, fillers, and plasticizers like polybutene are used to modify compound properties.<sup>43,44</sup> These compounds are applied by thermal pumping and dispensing systems designed for bulk, hot melt materials or by a semi-portable, heated extruder gun. Applications involve mainly in-plant assembly line sealing of prefabricated buildings and windows, household appliances, and automotive adhesive/sealant end uses where the compound can flow into place and serve both to adhere the substrates and to seal out the elements.

### SUPPLIERS OF TRADE NAMED FORMULATING INGREDIENTS

A-Fax 600	Hercules Inc.	Oppanol	BASF
AgeRite Resin D	R. T. Vanderbilt Company	Pentalyn H	Hercules Inc.
AgeRite White	R. T. Vanderbilt Company	Parapol® Polybutenes	Exxon Chemical Company
Atomite	ECC America Inc.	Piccolyte S-115	Hercules Inc.
Be Square 175	Petrolite Specialty Polymers Grp.	Poly DNB	Lord Corporation
Bromobutyl	Exxon Chemical Company; Polysar Limited	Polysar Butyl	Polysar Limited
Butyl Zimate	R. T. Vanderbilt Company	QDO	Lord Corporation
Cab-O-Sil M5	Cabot Corporation	Satinton W/Whitetex	Engelhard Corporation
Chlorobutyl	Exxon Chemical Company; Polysar Limited	Schenectady Resins	Schenectady Chemicals Inc.
DBQDO	Lord Corporation	Silanes	Union Carbide Corporation
Elvax 40	E. I. DuPont, Inc.	Silene 732D	PPG Industries, Inc.
Epolene C-10	Eastman Chemical Products Inc.	Staybelite Ester 10	Hercules Inc.
Escorene® EVA	Exxon Chemical Company	Vistanex® PIB	Exxon Chemical Company
Exxon Butyl	Exxon Chemical Company	Zirex	Reichhold Chemicals, Inc.
Escorez® Resins	Exxon Chemical Company		
Ethanox 702	Ethyl Corporation		
Finaprene 1205	Fina Oil & Chemical Company		
Hercolyn D	Hercules Inc.		
Irganox 1010	Ciba-Geigy Corporation		
Kalar	Hardman Inc.		
Kalene	Hardman Inc.		
Kraton 1107	Shell Chemical Company		
Laktane	Exxon Corporation		
Mistron Vapor Talc	Cyprus Industrial Minerals		

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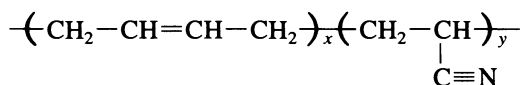
# Nitrile Rubber Adhesives

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## INTRODUCTION

Nitrile rubbers are broadly defined as copolymers of a diene and a vinyl unsaturated nitrile. This chapter will focus primarily on emulsion-polymerized copolymers of 1,3-butadiene and acrylonitrile, which represent the bulk of the commercially available nitrile elastomers. Commercial nitrile rubbers contain between 15 and 50% acrylonitrile, and have the following general structure:



Several excellent review articles describe nitrile rubber in great detail.<sup>1-6</sup> This chapter will also briefly discuss the solution-polymerized functionally terminated telechelic liquid copolymers of butadiene and acrylonitrile. The latter materials, though much smaller in commercial volume, are achieving increased importance in high performance adhesive systems.

Nitrile rubbers are compatible with phenol-formaldehyde resins, resorcinol-formaldehyde resins, vinyl chloride resins, alkyd resins, coumarone-indene resins, chlorinated rubber, hydrogenated rosins, coal-tar resins, epoxies, and other resins, forming compositions which can be cured and which can provide excellent adhesives of high strength, high oil resistance, and good resilience. Nitrile rubber cements are

easily adapted by proper formulation to many applications. Nitrile rubbers have been used to bond cured and uncured nitrile rubbers to themselves, to vinyls, to polychloroprene, and to other elastomers. They have been used for coating fabrics to provide oil resistance and wear resistance and to adhere vinyls and elastomers to fabrics. Blended with phenolic resins, they have been used for many applications. Nitrile rubbers have excellent compatibility as adhesives with polar adherends such as protein fibers, textiles, paper, and wood.

## PREPARATION OF NITRILE RUBBER

### Emulsion Technology

Commercial nitrile rubber is produced using an emulsion polymerization process. Emulsion polymerization systems are commercially attractive in that they allow the production of high molecular weight polymer at high polymerization rates. There are five major nitrile rubber producers that supply the U.S. market, including BFGoodrich, Uniroyal Chemical (recently sold to Avery International), Polysar, Goodyear, and Copolymer. Some of these suppliers have a very limited product line since they use a continuous manufacturing process. Other suppliers use a batch manufacturing process and offer a large number of products, e.g., the BFGoodrich product line contains approximately 70 different nitrile rubber products. A

list of all commercial nitrile rubbers would be quite lengthy. Table 1 lists the commercial "hot" nitrile rubbers since the hot rubbers are generally preferred in adhesive applications.

In an emulsion polymerization process, there are numerous variables that may be changed. Blackley's recent book<sup>7</sup> discusses emulsion rubber production and provides an outline of the mechanism of emulsion polymerization. Some of the major polymerization variables will be discussed here, as they affect the adhesive properties of the resulting polymers.

**Monomer Type/Level.** Typically, nitrile rubbers of greater than 25% acrylonitrile content are employed in cement/adhesive applications.<sup>8</sup> As the acrylonitrile level of nitrile rubber is increased from 15 to 50%, the polar nature of the polymer increases. This is reflected by a change in the solubility parameter (Fig. 1).

The second major effect of increasing the acrylonitrile content of nitrile rubber is an increase in the glass transition temperature. Glass transition temperatures for nitrile rubbers of homogeneous compositions may vary from approximately  $-60$  to  $-10^{\circ}\text{C}$  as the acrylonitrile content is increased from 15 to 50%, respectively. However, it is also well known that

many nitrile elastomers of  $<35\%$  acrylonitrile content are not homogeneous compositionally, but instead exist as mixtures of copolymers with variable acrylonitrile contents. This has been shown to produce incompatible polymer mixtures that exhibit two glass transition temperatures.<sup>9-11</sup>

Through the years other monomers have been investigated. The diene commonly employed is 1,3-butadiene, although isoprene, 2-ethyl butadiene, 2,3-dimethyl butadiene, piperylene, and other substituted dienes have been investigated. The nitrile commonly employed is acrylonitrile. It has been reported that when part of the acrylonitrile is replaced by methacrylonitrile or ethacrylonitrile, the cement-making properties of the rubber are improved.<sup>6</sup> Small proportions of a third monomer may also be used in conjunction with the two principal components. Hycar 1072, which employs methacrylic acid as the third monomer, is occasionally used in adhesive applications. Other monomers including ethyl acrylate, methyl methacrylate, styrene, vinylidene chloride, acrylic acid, N-vinyl-2-pyrrolidone, and vinyl acetate have been employed in varying amounts to adjust the adhesive and elastomeric properties.

**Table 1. Hot Nitrile Rubbers.**

<i>Supplier</i>	<i>Trade Name</i>	<i>% Acrylonitrile</i>	<i>Nominal Mooney Viscosity</i>	<i>Remarks</i>
BFGoodrich	Hycar® 1000X88	43	80	cement grade
	Hycar 1001CG	41	87	
	Hycar 1002	33	85	
	Hycar 1022	33	48	directly soluble
	Hycar 1014	21	80	
	Hycar 1312LV	26	10,000 cp <sup>a</sup>	liquid
	Hycar 1422X5	33	48	ground form of 1022
Uniroyal Chemical (Avery International)	Paracril® CJ	38.5	47	crumb form
	Paracril C	35	75	
	Paracril CV	35	65	
	Paracril B	29.5	80	
	Paracril AJ	23.5	50	
	Paracril 1880	22	75	
Goodyear	Chemigum® N3	39	84	
	Chemigum N5	39	87	
	Chemigum N6B	33	54	
	Chemigum N7	33	86	

<sup>a</sup>Brookfield viscosity.



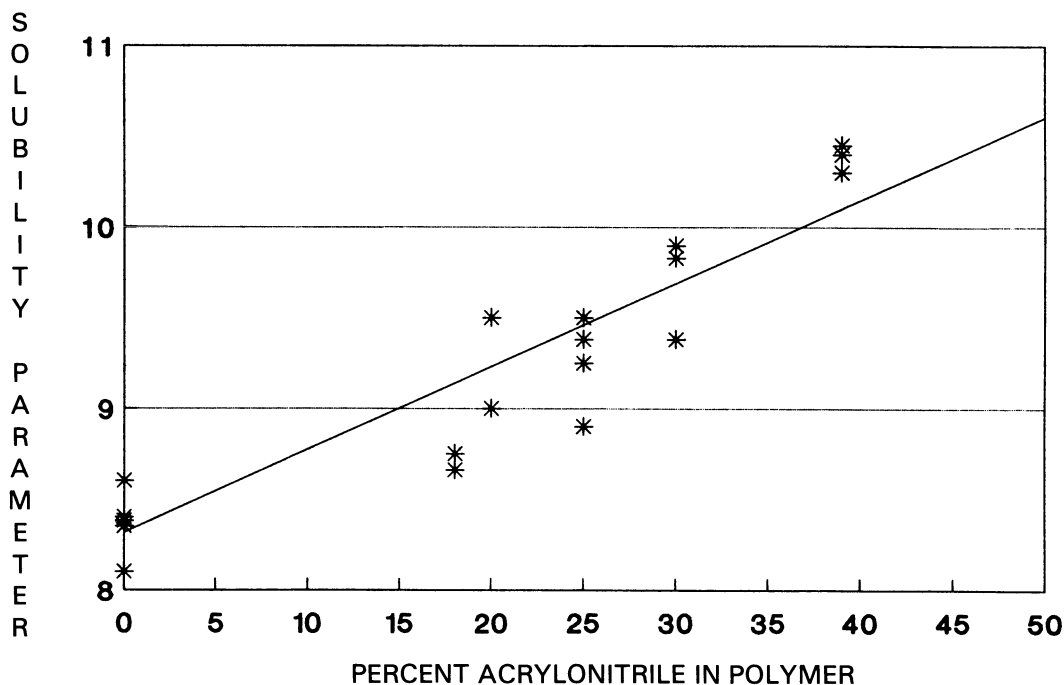
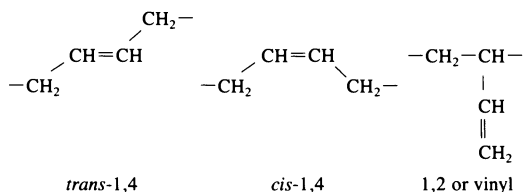


Fig. 1. Solubility parameter vs. percentage acrylonitrile nitrile rubbers.

**Polymerization Temperature—Hot vs. Cold.** Most commercial nitrile rubber production today is conducted at a polymerization temperature of 5°C (41°F) and is referred to as *cold* rubber. Cold rubber, with its improved processing properties, is generally preferred for applications where mixing, calendering, or extruding are encountered.<sup>5</sup> However, in adhesive applications, *hot* nitrile rubbers are generally preferred (although not exclusively). Hot polymerizations are conducted at temperatures of 25–50°C. Hot polymers tend to exhibit higher levels of branching and a slightly higher *cis*-1,4 microstructure for the butadiene segments. Infrared spectroscopy has been utilized to analyze nitrile elastomers for their microstructural architecture,<sup>12</sup> since it is well known that three different structures can exist for the butadiene segments:



**Emulsifier Type/Level.** Nitrile rubbers are polymerized with anionic emulsifiers.<sup>4</sup> A large number of anionics can be used as primary emulsifier including: the sodium, potassium, or ammonium salts of fatty acids, rosin acids, alkyl sulfates, and alkyl aryl sulfonates. Since emulsifier residues remain in the nitrile rubber after the latex is coagulated and dried, it has been found that the type and level of emulsifier used can affect the adhesive properties.

**Molecular Weight Modifier.** In order to control the molecular weight of the polymer, various molecular weight modifiers or chain transfer agents are used. These modifiers are frequently aliphatic mercaptans and, occasionally, diisopropyl xanthogen disulfide. Without a modifier, a very high molecular weight polymer would result with undesirable branching and, as a result, extremely poor processing characteristics. It has been reported that the use of dimethyl xanthogen disulfide produces an emulsion nitrile rubber with superior adhesive properties compared to a nitrile rubber prepared with a *n*-dodecyl mercaptan.<sup>13</sup> For ad-

hesive and sealant applications where a very low molecular weight nitrile rubber is desired, high levels of molecular weight modifier are used to produce a viscous, liquid polymer. Liquid nitrile rubbers, e.g. Hycar 1312, are useful as tackifier agents.

#### **Conversion of Monomer to Polymer.**

Commercial nitrile rubber polymerizations are typically run to final conversions (of monomer to polymer) between 75 and 90%. As conversion increases, the resulting polymer is more highly branched and crosslinking or gel formation is increased. If a gel-free or clear cement is desired, lower conversions need to be employed, since the solubility of the nitrile copolymer is dependent on the ultimate conversion and molecular weight.

**Batch vs. Continuous.** Some nitrile rubber producers use a batch process. The batch process has the advantage of making small amounts of many different products, thus enabling the producer to tailor-make polymers for relatively low-volume specialty applications. Obviously, however, the disadvantage is the relatively high changeover costs. On the other hand, some nitrile rubber producers use a continuous process. This process is relatively low cost but limits the number of products that can be economically produced since minimum run quantities are relatively large.

The copolymerization kinetics are such that nitrile rubbers produced at a polymerization temperature of 5°C have an azeotropic composition of 42.5% acrylonitrile.<sup>5</sup> In other words, the composition of the monomer feed and the copolymer produced will be equal and constant as the polymerization conversion increases. On the other hand, hot polymerization conditions (50°C) have an azeotropic composition of 37.5% acrylonitrile. In either case, if a batch polymerization is conducted at a composition which differs from the azeotropic mixture, the composition of the nitrile rubber formed will vary as a function of conversion. This effect is especially pronounced for low acrylonitrile levels, which are relatively far from the azeotropic composition. Continuous production methods meter in the faster reacting monomer in order to keep the monomer and

polymer compositions constant. As a result, batch and continuous production methods can produce nitrile rubbers with different sequence distributions (arrangement of the monomer units) which affect their properties in adhesive applications.

**Coagulation and Drying.** Since residual nonpolymer components (emulsifier, coagulant, antioxidant, electrolyte, etc.) can affect the adhesive properties of a nitrile rubber, the method of coagulation, washing, and drying of the latex is important. Common coagulants include aluminum sulfate and calcium chloride, although other materials are also used. The conditions employed to wash the coagulated crumb rubber and any mechanical squeezing of the wet rubber crumb will also affect the residual level of emulsifier and coagulant.

**Grinding.** As a final production step, some nitrile rubbers are ground to a particulate form. The larger surface area of these products makes them more readily soluble and, as such, often desirable in cement applications. To prevent reagglomeration of these products an anti-cake or dust must be added. Soapstone, talc, resins, powdered polymers, or other materials are used for this purpose and may ultimately affect the performance of the adhesive.

#### **Functionally Terminated Telechelic Liquid Polymers**

As mentioned in the introduction, there is a new class of butadiene acrylonitrile copolymers that has found increasing utility in various adhesive systems. These polymers are terminally functional (telechelic) liquids. The preparation of these materials varies significantly from the normal emulsion polymers. These materials are solution polymerized with a suitable initiator/chain transfer agent that results in a nearly difunctional molecule. These polymers have number average molecular weights in the range of 3,500. Polymers with acrylonitrile contents from 10 to 27% are commercially available. If increased functionality is required, pendent groups can be introduced into the backbone by copolymerization with small amounts of a carboxyl-containing monomer. The terminal func-

**Table 2. Hycar Reactive Liquid Polymers.**

	<i>1300X8</i> <i>CTBN</i>	<i>1300X9</i> <i>CTBNX</i>	<i>1300X13</i> <i>CTBN</i>	<i>1300X21</i> <i>ATBN</i>	<i>1300X16</i> <i>ATBN</i>	<i>1300X22</i> <i>VTBN</i>	<i>1300X23</i> <i>VTBNX</i>	<i>1300X17</i> <i>VTBNX</i>
Acrylonitrile content, %	18	18	26	10	16	16	16	16
Functionality	carboxyl	carboxyl	carboxyl	2° amine	2° amine	acrylated	acrylated	1° hydroxyl
Brookfield viscosity, centipoise @ 27°C	135,000	160,000	570,000	180,000	200,000	225,000	250,000	140,000
Specific gravity	0.948	0.955	0.960	0.938	0.956	0.984	0.985	0.960
Equivalent weight	1,920	1,490	1,750	1,200	900	1,400	1,100	1,880

tionality can be manipulated to give carboxyl groups, secondary amine groups, primary hydroxyl groups or acrylate groups. Table 2 lists the major commercially available materials.<sup>14</sup>

These reactive liquid polymers differ significantly from the older high molecular weight analogs in several important aspects. First, since they are nearly difunctional, they can easily be reacted with other polymers or prepolymers to give high molecular weight materials containing short nitrile rubber blocks in the backbone. The variety of functional groups enables these materials to react with many other materials including epoxy, polyester, and polyurethanes. Secondly, these materials are viscous liquids at room temperature and can be mixed with other liquid materials such as epoxies to yield a 100% active liquid system. This allows the formulator or end user to avoid the use of volatile solvents and the associated environmental emission problems. Thirdly, since these materials are solution-polymerized, the end product can be easily produced virtually free of inorganic salt contamination. This is particularly important in areas such as printed circuit boards where very small amounts of mobile ions can destroy the electrical characteristics of the adhesive or encapsulant.

## COMPOUNDING NITRILE RUBBER CEMENTS

### Polymer Selection and Solubilization

There are numerous nitrile rubbers used in cement and adhesive applications, although some general trends may be noted:

- High acrylonitrile levels are frequently used. Superior bonding and film properties are obtained from high acrylonitrile containing nitrile rubbers.

- High Mooney viscosities are preferred. A good indication of the potential bond strengths obtainable from nitrile rubbers is given by the Mooney viscosity of the raw polymer. In general, the higher the Mooney viscosity, the higher the strength of the cement adhesive.
- Hot-polymerized nitrile rubbers are often preferred. However, this is not always the case; e.g., cold-polymerized Hycar VT455 and Hycar VT480 are finding significant application in the adhesive area.

Depending upon the particular nitrile rubber that is selected, it may or may not require milling prior to cement preparation. Details concerning the milling and processing of nitrile rubbers are available in suppliers' bulletins<sup>8,15</sup> and literature reviews.<sup>5,6</sup> Milling on tight, cold mill rolls is probably the most efficient method of breaking down nitrile rubbers and rendering them soluble. Nitrile rubbers and their compounded stocks, prepared for cement use by milling, should be put into solution as soon as possible after milling since solubility is progressively lost with time. Even though some nitrile rubbers are directly soluble, milling can be employed to reduce the cement viscosity. The effect of milling on the viscosity and shelf stability of nitrile rubber cements is shown in Table 3.<sup>8</sup>

Sarbach and Garvey<sup>16,17</sup> studied the solubility of nitrile rubber in eighty typical solvents. They concluded that such rubbers are soluble in aromatic hydrocarbons, chlorinated hydrocarbons, ketones, esters, and nitroparaffin compounds, and are insoluble in aliphatic hydrocarbons, hydroxyl compounds, and acids. Among the solvents commonly employed with nitrile rubbers, where rapid evaporation is desired, are acetone, methyl ethyl ketone, chlo-

**Table 3. Effect of Milling on Viscosity and Shelf Stability of Cements.**

<i>Recipe No.:</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>
Hycar 1041	20.0	20.0	—	—
Hycar 1042	—	—	20.0	20.0
Methyl ethyl ketone	80.0	80.0	80.0	80.0
Totals	100.0	100.0	100.0	100.0
Treatment	Milled	Unmilled	Milled	Unmilled
LVF Brookfield Viscosity, cps (#4 spindle, 30 rpm)				
Initial	1,200	Gel	940	2,380
24 hr	1,200	—	940	2,380
48 hr	1,200	—	1,080	2,800
72 hr	1,200	—	1,080	2,940
144 hr	1,200	—	1,080	3,300

roform, ethylene dichloride, ethyl acetate, and trichloroethylene. Slower evaporating solvents include nitromethane, nitroethane, the nitropropanes, dichloropentenes, chlorobenzene, chlorotoluene, methyl isobutyl ketone, butyl acetate, and methyl chloroform.

Cements of 20–35% total solids are easily obtainable in methyl ethyl ketone and chlorinated solvents. Nitroparaffins may be used as solvents when highly concentrated cements (up to 50% total solids) are desired.<sup>18</sup> (In general, the more concentrated the nitrile rubber ce-

ment, the poorer its stability). It has been reported that 1-chloro-1-nitropropane<sup>19</sup> is effective in stabilizing nitrile rubber solutions.

Final selection of a solvent for a nitrile rubber cement will be determined, in addition to effective solvent action, by such factors as availability, cost, toxicity, odor, flammability, and rate of evaporation. Some solvent mixtures which have been recommended for use with nitrile rubbers to achieve a desired balance of cost, evaporation rate, and good solvent action are given in Table 4. Since many of these sol-

**Table 4. Solvent Mixtures for Hycar Rubber (percentages by volume).**

<i>Two-Component Mixtures</i>		<i>Three-Component Mixtures</i>	
1. Nitroethane or nitromethane	10–30%	1. Chlorotoluene	10–20%
Benzene, toluene, or xylene	90–70%	Nitroethane	10–20%
		Benzene	80–60%
2. Ethylene dichloride	10–30%	2. Ethylene dichloride	10–20%
Benzene, toluene, or xylene	90–70%	Chlorobenzene	10–20%
		Methyl ethyl ketone	80–60%
3. Chlorotoluene or chlorobenzene	10–30%	3. Butyl acetate	33 $\frac{1}{3}$ %
Benzene, toluene, or xylene	90–70%	Chlorobenzene	33 $\frac{1}{3}$ %
		Acetone	33 $\frac{1}{3}$ %
4. Chlorobenzene	10–30%	4. Ethylene dichloride	10%
Methyl ethyl ketone	90–70%	Toluene	10%
		Benzene	80%
5. Nitroethane	10–30%	5. 1-Nitropropane	25%
Methyl ethyl ketone	90–70%	Acetone	50%
		Benzene	25%
6. Chlorotoluene	10–30%		
Diisopropyl ketone	90–70%		

vents are toxic, cements and adhesives containing them should always be prepared and used in well ventilated and preferably hooded areas.

### Types of Compounding Ingredients

Nitrile rubbers may be compounded for many cement applications. Normal rubber compounding techniques should be employed, including the types of compounding ingredients described below.

**Pigments.** Pigments are added to nitrile rubber cements for a variety of purposes. A major reason to add pigments is for their reinforcing qualities; other reasons include promotion of tack, extension of storage life, improvement of heat resistance, and reduction of cost. Carbon blacks enhance the strength of cured nitrile rubber films. The best properties are obtained with channel black, usually added in amounts of 40–60 parts (based on 100 parts nitrile rubber). Softer furnace blacks give lower tensile properties with a slight loss in adhesion, but provide longer shelf life and somewhat lower costs. Among the nonblack pigments, iron oxide, zinc oxide, hydrated silica, titanium dioxide, and clays are the most commonly employed. Iron oxide is commonly used at levels of 75–100 parts per hundred rubber (phr). It yields smooth cements of relatively high tensile strength, improved tack and storage life, but lacking good abrasion resistance. Zinc oxide (25–50 phr) improves tack but not film strength. Hydrated silica (20–100 phr) is used to improve tensile strength where blacks are objectionable and is especially useful in fabric adhesions, although excessive loadings tend to reduce adhesion. Titanium dioxide (5–25 phr) is used to impart whiteness, promote tack, and extend storage life. Clays are employed to reduce cement costs at the expense of tensile strength and adhesion.

**Plasticizers.** Softeners are sometimes employed with nitrile rubbers to improve tack and adhesive properties. They are added to high nitrile content rubbers to aid processability. Commonly employed in cement applications are esters (e.g., dibutyl phthalate, dioctyl phthalate, tricresyl phosphate, tributoxyl ethyl phosphate, dibenzyl sebacate), ester gums,

alkyd resins, coumarone-indene resins, liquid nitrile rubbers, coal-tar resins, etc.

**Curatives.** Curing agents are used with nitrile rubbers when high strength and especially strength at elevated temperatures is a requisite of the adhesive. The usual cure packages (curatives, accelerators, activators, etc.) employed in dry nitrile rubber compounding are applicable for curing nitrile rubber cements. Sulfur/benzothiazyl disulfide/zinc oxide (2/1.5/5) is a common system. When low temperature curing cements are desired, ultra accelerators such as the zinc salts of the thiuram disulfides or accelerators activated by aldehyde-amine complexes may be used. Preferably, these are incorporated just before use of the cement.

**Tackifying Agents/Resins.** High strength, oil resistant, resilient adhesives are prepared with nitrile rubbers by modification with resins and other rubbers. The phenolic resins are extensively employed for this purpose. Resorcinol-formaldehyde resins, polyvinyl chloride resins, and alkyd resins have also been employed. “Vinsol” resin, hydrogenated rosin and its derivatives, coal-tar resins, coumarone-indene resins, and liquid nitrile rubber (e.g., Hycar 1312) are useful tackifying agents. Chlorinated rubber has been used to improve tack, stability, and adhesion to a variety of materials, including metals. Tack and adhesive properties of nitrile rubbers have been improved for some applications by the inclusion of chlorinated alkyl carbonates such as chlorinated dibutyl carbonate.<sup>20,21</sup>

**Antioxidants.** All nitrile rubber producers add an antioxidant to their raw nitrile rubbers. However, where heat resistance and the maximum in durability and service is demanded, additional antioxidant may be added to the cement. Antioxidants commonly used in nitrile rubbers (e.g., amine antioxidants) may be used if staining is not a factor. Antioxidants may also contribute stability and tack.

**Thickening Agents.** Thickening agents are sometimes added to nitrile rubber cements to give them desired pseudoplasticity wherein ap-

parent viscosity decreases rapidly with increase in rate of shear. This property, together with a high yield value, is very desirable for cements to be employed in spreadcoating operations. Such properties also tend to prevent excessive strike-through during spread coating. Low total solids, low viscosity solvent cements can be thickened to usable viscosities. Such thickening agents are also employed to improve the properties of spray-type cements, especially where thick coatings are desired. A carboxylic vinyl polymer, Carbopol® 934, has been very effective for thickening nitrile rubber cements based on methyl ethyl ketone.<sup>8,22</sup>

## APPLICATIONS

Nitrile polymers have found a varied number of applications in the adhesive area. These applications are based on the excellent elastomeric properties of the polymer coupled with its polarity which gives the material good solvent resistance and compatibility with other polar materials. The various commercially available physical forms of nitrile polymers (slab rubber, crumb rubber, liquid rubber and latex) have also increased the ease of processing of the material and broadened the application base. In an attempt to review this broad area, the applications have been subdivided into three parts. In the first section applications involving solely nitrile rubber as the base polymer as well as miscellaneous nitrile rubber blends are reviewed. Due to the large number of applications involved, nitrile rubber/phenolic blends have been separated into the second section. For the same reason, nitrile rubber/epoxy blends are covered separately in the third section.

### Nitrile Rubber Systems

**Laminating Adhesives.** Nitrile rubbers have found a large number of applications in the area of laminating adhesives. Table 5 lists the varied applications for these adhesive systems. Several of these specific application areas will then be covered in more detail. Polyvinyl chloride, polyvinyl acetate, and other polymeric films have been laminated to a wide variety of metals including aluminum and brass.

**Table 5. Applications for Laminating Adhesives of Nitrile Rubber.**

Unvulcanized nitrile to:	Leather to:
Unvulcanized nitrile	Leather
Rayon	Vinyl
Cotton	Composition sole
Nitrile to:	Synthetic rubber sole
SBR	Cotton
Neoprene	Vinyl film to:
Leather	Vinyl film
Nylon	Cotton
Teflon	Vinyl
Steel	Vinyl to vinyl foam
Brass, tin plate	Cork to cork
Aluminum	Glass to glass
Nylon to nylon	Wood to wood
Orlon to Orlon	Grit to polyurethane foam
Cotton to cotton	Copper to:
	Phenolic board
	Epoxy board
	Asphalt board to mohair fabric

The polymeric film and the metal are coated with an adhesive shown in Table 6. The resulting laminates are pressed together under 200 psi pressure at 300°F for 15 minutes.<sup>23</sup>

Cellulose acetate flock has been adhered to textile materials to make a pile surface using the cement composition shown in Table 7.<sup>24</sup>

Cements of nitrile rubber and Vinsol ester gum<sup>25</sup> in ethylene dichloride or a similar solvent have been recommended as adhesives and surface coatings. An adhesive for leather and shoe fabrication has been formulated from blends of nitrile rubber, pyroxylin,<sup>26,27</sup> and other ingredients such as sulfur, zinc oxide, and calcium silicate. A room temperature adhesive for vulcanized rubber to rubber having excellent initial adhesive strength and oil resistance was prepared from a high acrylonitrile hot polymerized nitrile rubber (e.g., Hycar 1001CG),

**Table 6. Laminating Adhesive for Polymeric Films to Metals.**

Hycar 1002	150
Vinyl chloride-vinylidene chloride co-polymer	50
Diocetyl phthalate	20
Paraplex G-30	10
Barium Stabilizer (e.g., Staflex QXMA)	6
Sulfur	1
Benzothiazolyl disulfide	1

**Table 7. Adhesive for Cellulose Acetate Flock.**

Hycar 1002	100
Sulfur	3
Mercaptobenzothiazole	2.4
Phenyl guanidine	0.6
Zinc oxide	7.5
Coumarone resin	37.5
Dimethyl phthalate	300
Bis-(2-ethylhexyl)phthalate	45
Methyl ethyl ketone	378
Methyl isobutyl ketone	256

carbon black and a large amount of zinc dithiocarbamate.<sup>28</sup>

A blend of Hycar 1432 and chlorinated poly(4-methyl-1-pentene) in a ratio of 3 to 1 was found to give excellent adhesive properties for bonding a plasticized PVC sheet to steel.<sup>29</sup> A PVC impregnated conveyor belt carcass was bonded to a layer of unvulcanized neoprene rubber.<sup>30</sup>

Nitrile rubber adhesives have been used to bond medium-to-high polarity rubbers with polyamide substrates. In an early work, nitrile rubber in solvent was treated with 10–20 parts of phosphoric acid at 50–100°C and subsequently neutralized.<sup>31</sup> In more recent work, acrylic acid, methacrylic acid, dicumyl peroxide and phenol ether were added to a mixture of nitrile and formaldehyde-phenol oligomer to give a rubber-to-polyamide adhesive.<sup>32</sup>

The adhesive properties of nitrile rubber can be further improved by chemical modification. Nitrile rubber treated with isocyanate was mixed with a polyisocyanate<sup>33</sup> and found to be an excellent adhesive for rubber to sailcloth laminates. In other work, methyl methacrylate was grafted onto nitrile rubber<sup>34</sup> to give a material with good adhesive strength.

Nitrile rubber which is commercially available as a latex has also found widespread use in adhesive applications. The distinct advantage to the latex form is that the material can be spread on the substrate directly without first dissolving the polymer with solvent. This is very advantageous to formulators that can not handle the environmental aspects of later removing the large amounts of hydrocarbon diluent.

Medium high acrylonitrile latices like Hycar 1552 or carboxylated acrylonitrile butadiene latices like Hycar 1572 have been found to give good bond strength to fabric–vinyl foam laminates without altering the desirable characteristics of the fabric. Normally the latex is first thickened with a sodium polyacrylate before use. The nitrile latex gives a laminate which is softer and more flexible than the corresponding laminate made with the carboxylated polymer.<sup>35</sup>

A medium high acrylonitrile latex in combination with an emulsion of a liquid nitrile rubber has been found to be an excellent adhesive for sculptured styrene foam sections. Such an adhesive provides excellent “wet grab” and thus need not be entirely dried to realize optimum adhesive properties. A stable emulsion of the liquid nitrile is made by first adding a polyacrylate thickening agent to water. Normally a high shear mixer like an Eppenbach is employed to insure good dispersion. The polyacrylate is then neutralized with ammonium hydroxide and finally the liquid nitrile is added to this solution. A typical composition for the liquid nitrile emulsion is given in Table 8. The final adhesive would contain one part of nitrile latex and six or more parts of liquid nitrile emulsion.

A medium high acrylonitrile latex can be compounded with a resorcinol-formaldehyde solution to give a good adhesive to bond nitrile rubber stocks to cotton or rayon fabric. This treatment results in adhesion as good or better than that obtained by saturation of the fabric with solvent cement. A typical recipe is shown in Table 9.<sup>35</sup> This adhesive would be cured for 1–5 minutes at 160°C.

Nitrile latices have also found applications in adhering fabric backed vinyl wall covering to SBR foam. Nitrile latices can be used to give effective adhesion of Saran film to food pack-

**Table 8. Recipe for Stable Liquid Nitrile Emulsion.**

Hycar 1312	99.25
Polyacrylate resin (e.g., Carbopol 934)	0.60
Ammonium hydroxide (20%)	0.14
Water	100.00

**Table 9. Adhesive for Nitrile Rubber to Cotton or Rayon.**

	Dry Wt.	Wet Wt.
Nitrile latex (e.g., Hycar 1562X102)	85	212
6.5% Resorcinol formaldehyde solution	15	231
Water for dilution	—	57

aging paper. Such an adhesive maintains integrity under heating, immersion, and vacuum.<sup>35</sup>

A very versatile adhesive for manufacture of a wide variety of laminates can be made by mixing a nitrile latex with Vinsol, a high melting thermoplastic resin from Hercules Inc. The Vinsol resin, which is compatible with most nitrile latices, provides the following advantages:

1. Improved surface wetting and penetration.
2. Improved specific adhesion to metal surfaces.
3. Reduced moisture vapor transmission of the adhesive film.
4. Improved water resistance with no loss in resistance to liquid hydrocarbons.
5. Reduced cost.

Nitrile latex can be mixed with PVC latex to give excellent adhesion of polypropylene carpet and plywood backings. The formulation shown in Table 10 was found to give good adhesion even after seven days immersion in water.<sup>35</sup>

Combinations of nitrile latices and styrene-butadiene latices give good laminating bonds for saturated paper and woven fabrics. A potential application is soft-shell luggage with multiply construction. Finally, nitrile latex in combination with various other polymers has been shown to be a good adhesive for bonding polyurethane foam to concrete.<sup>36</sup>

**Table 10. Adhesive to Laminate Polypropylene Carpet to Plywood.**

	Total Solids	Dry Parts
Hycar 1562X103	41.0	1250
Geon 450X20	55.0	500
Picconol A600E	55.0	750
Acrysol GS	5.0	25
Toluene	100.0	125
Dixie clay dispersion	65.0	750

**Cements of High Tack.** Cements of high tack can be produced by formulating the material to include tackifying and plasticizing agents combined with large amounts of zinc oxide. Table 11 contains an illustrative example of such a formulation. A liquid nitrile such as Hycar 1312 may also be used to enhance tack.

The high-tack cement in Table 11 would be prepared by dissolving 1,400 grams of formulation A in  $\frac{1}{2}$  gallon of chlorotoluene and then diluting this mixture to one gallon with chlorobenzene. Likewise 1,400 grams of formulation B would be dissolved in  $\frac{1}{2}$  gallon of chlorotoluene and then diluted to one gallon with chlorobenzene. Just before using equal volumes of the two solutions would be mixed.<sup>8</sup>

**Spreading Compounds.** Spreading compounds are recommended for maximum resistance to gasoline and oil combined with good low temperature flexibility (Table 12).<sup>8</sup>

**White Cement Formulation.** In some cases it may be desirable to formulate a cement with white pigmentation. This can be done with titanium dioxide, silica or similar materials (Table 13). Just before use add four parts of Butyl

**Table 11. High-Tack Cement.**

	Part A	Part B
Hycar 1001 CG	100.0	100.0
EPC black	10.0	10.0
Zinc oxide	150.0	150.0
AgeRite Resin D	5.0	5.0
Refined coal tar (BRT-7)	35.0	35.0
Benzyl alcohol	18.0	18.0
Dibutyl metacresol	35.0	35.0
Sulfur	5.0	
Butyraldehyde-aniline (Accelerator 808)	—	8.0



**Table 12. Spreading Compounds Using Nitrile Rubber.**

	1 <sup>a</sup>	2 <sup>b</sup>	3 <sup>c</sup>	4 <sup>c</sup>
Hycar 1001CG	100.0	100.0	—	—
Hycar 1042	—	—	100.0	100.0
Zinc oxide	5.0	5.0	5.0	5.0
Spider sulfur	2.0	2.0	1.5	1.5
N770, SRF-HM black (Sterling S)	75.0	60.0	75.0	75.0
Triacetin	35.0	—	—	—
Litharge	—	10.0	—	—
AgeRite Resin D	—	2.0	—	—
Diocetyl phthalate	—	25.0	—	—
Flexricin P-4 Baker Castor Oil	—	—	10.0	10.0
Synthetic resin extender (Turpol 1093)	—	—	—	20.0
Benzothiazyl disulfide (Altax)	1.5	—	1.5	1.5
Stearic Acid	—	—	1.0	1.0
Total	218.5	204.0	194.0	214.0

<sup>a</sup> Dissolve 675 grams in one quart of nitromethane and make up to one gallon with Solvesso No. 1.

<sup>b</sup> Make up as a 45% total solids solution in ethylene dichloride and then dilute to a 25% total solids solution by adding methyl ethyl ketone.

<sup>c</sup> The spreading compound (see A and B below) is made from blends of the two compounds by weighing small pieces into quart cans adding methyl ethyl ketone and rolling for 24 hours.

	A	B
Compound No. 3	194.0	—
Compound No. 4	—	214.0
Methyl ethyl ketone	776.0	642.0
Total	970.0	856.0

Eight (activated dithiocarbamate, R. T. Vanderbilt Co.) as a 5–10% solution in MEK.<sup>8</sup>

Similar nonblack cements have been suggested<sup>37</sup> for the adhesion of cotton, wood, paper, compositions, leather, and nuclear shoe soling. Leather adhesives<sup>38,39</sup> have been formulated from nitrile rubbers using the composition shown in Table 14.

**Structural.** Many of the applications of nitrile rubber in the structural adhesive area in-

volve blends with either phenolic or epoxy resins. These will be covered in detail in the next two sections.

Besides phenolic and epoxy blends, there are other structural applications of nitrile rubber noted in the literature. A two-component adhesive for zinc-plated substrates has been described<sup>40</sup> with a significant amount of nitrile rubber in both parts.

Another example of a structural adhesive is a two-part solventless liquid system. One part contains carboxylated nitrile rubber, methyl methacrylate, and cobalt naphthenate. The second part is composed of carboxylated nitrile rubber, methyl methacrylate, and cumene hydroperoxide. In this example the carboxylated nitrile rubber used was Hycar 1072.<sup>41</sup>

**Table 13. Typical White Cement Formulation.**

Hycar 1022 polymer	100.0
Zinc oxide	5.0
Sulfur	1.5
Titanium dioxide (Titanox)	15.0
Hydrated silica (HiSil)	25.0
Chlorinated paraffin wax (Chlorowax 40)	10.0
Tetramethylthiuram monosulfide (Unads)	0.4
Stearic acid	1.0
Total	157.9

Mix to 15% total solids in MEK.

**Table 14. Nitrile Leather Adhesive.**

Nitrile rubber	100.0
Vinyl chloride-vinyl acetate polymer	100.0
Zinc oxide	5.0
Stearic acid	1.5
Calcium silicate	2.0
Solvent	600–800

**Hot Melt Adhesives.** Nitrile rubbers can be used in combination with thermoplastic polymers to give a hot melt adhesive. Liquid nitrile rubber (Hycar 1312) was added to an acrylic acid-ethylene copolymer. The resulting hot melt adhesive gave a bond strength between aluminum plates of 11.9 lb/in. vs. 5.1 lb/in. for the same thermoplastic adhesive without the liquid nitrile rubber.<sup>42</sup>

### Nitrile Rubber/Phenolic Adhesives

Nitrile rubber and a phenolic resin have been used together in many adhesive applications. Equal parts by weight of a nitrile rubber and a phenolic resin (e.g., Durez 12687) in a suitable solvent (e.g., methyl ethyl ketone) at a total solids level of 20–30% is suitable for many adhesive purposes. Commonly, 30–100 phr of phenolic resin is employed. Some indication of the bond strength developed by such adhesives is shown in Table 15.<sup>8</sup>

The more phenolic resin employed, the greater the bond strength and the more brittle the adhesive. The increase of bond strength with resin content for nitrile rubber/phenolic resin cements is illustrated by the data in Table 16.<sup>43</sup> The rubber and resin were dissolved separately in methyl isobutyl ketone as 20% total solids solutions and then blended. The adhesive was coated on steel and the cloth was bonded after tack developed.

When preparing nitrile rubber/phenolic adhesives, the higher the nitrile content of the rubber, the greater its compatibility with phenolic resins. High acrylonitrile content rubbers thus produce adhesives with superior bonding and film properties, although lower acrylonitrile content rubbers will produce adhesives with better low temperature properties. Table 17 illustrates the effect of acrylonitrile content on the tensile properties of nitrile rubber/phenolic resin blends.<sup>15</sup>

Some of the more important applications for nitrile rubber/phenolic adhesives are described below.

**Printed Circuit Board Manufacturing.** In the last ten years there has been an increasing number of literature references to the use of ni-

trile rubber/phenolic adhesives in the manufacture of printed circuit boards. Much of this work is being done in Japan; two of the more active participants are Hitachi Chemical Co.<sup>44–52</sup> and Toshiba Corp.<sup>53–59</sup>

These patents discuss various adhesive formulations and techniques which may be employed to prepare printed circuit boards. Laminates are electrolessly plated with copper to produce these heat resistant boards. As an example, a Toshiba patent<sup>53</sup> describes hot pressing prepregs with films coated with adhesives to make such laminates (Table 18).

### Bonding Metal to Various Rubbers, Abrasives, Polyamide, and to Other Metals.

Various literature references discuss the use of nitrile rubber/phenolic adhesives for the bonding of metals.<sup>60–65,15</sup> Tanaka<sup>63</sup> discussed a two part liquid adhesive system based on solutions of nitrile rubber dissolved in methyl methacrylate. Aluminum plates were bonded together with the resulting adhesive. Kubo<sup>65</sup> reported that the adhesive composition of Table 19 was good for bonding steel plates.

Nitrile rubber/phenolic adhesives are also quite useful in adhering rubber to various metals,<sup>66–69</sup> e.g., in the manufacture of rubber covered metal rollers. Huber<sup>68</sup> reported that a nitrile/phenolic adhesive composition provided excellent bonding of rubber to a magnesium roll (Table 20). Other metal bonding applications with nitrile rubber/phenolic adhesives include laminating aluminum foil to paper and then to wood,<sup>70</sup> bonding abrasives to metal,<sup>71</sup> and bonding polyamide to metal.<sup>72</sup>

**Structural Adhesives.** Films of nitrile rubber/phenolic resins (i.e. tapes) have been employed in the aircraft industry for bonding metal to metal surfaces in both plain and honeycomb sandwich constructions. Several Wright Air Development Center reports<sup>73–77</sup> describe in detail the preparation of a nitrile rubber/phenolic resin tape, the metal surface preparation methods, and the methods of evaluating structural adhesives of this type. A formulation for a high-temperature liquid phenolic resin adhesive suitable for structural fabrication is given in Table 21.<sup>73</sup>

**Table 15. Hycar/Phenolic Cement-Adhesion Tests.**

	<i>1</i>	<i>2</i>	<i>3</i>
Hycar 1001CG	100	100	—
Durez 12687	50	100	100
Hycar 1022	—	—	100
Totals	150	200	200
<i>Adhesion, Pounds per Inch</i>			
Cotton duck to cotton duck (#633)	20	5	5
Cotton duck to cotton duck (#674)	5	5	4
Nylon to nylon (#936)	5	2	2
Nylon to nylon (#937)	6	6	5
Cotton duck #633 to wood	20	18	15
Cotton duck #674 to wood	18	15	25
Nylon #936 to wood	9	7	9
Nylon #937 to wood	7	10	10
Wood to wood (yellow pine)	387	619	641
Wood to cured Hycar 1022	35	12	23
Wood to cured acrylic rubber	25	12	10
Wood to cured natural rubber	15	25	20
Wood to cured SBR	10	5	6
Wood to steel	1400	1245	1360
Wood to brass	1000	930	1230
Wood to aluminum	860	758	883
Hycar to Hycar 1022 (cured)	33	28	30
SBR to SBR (cured)	6	18	25
Uncured Hycar 1022 compound to:			
Aluminum	5	4	3
Brass	28	23	18
Steel	5	5	3
Uncured acrylic rubber compound to:			
Aluminum	8	10	4
Brass	23	20	21
Steel	17	18	20
Uncured natural rubber compound to:			
Aluminum	9	7	6
Brass	21	25	18
Steel	12	20	20
Uncured SBR compound to:			
Aluminum	1	0	0
Brass	1	0	0
Steel	1	0	1

In addition to aircraft applications, adhesives of this type are employed in the bonding of friction materials (e.g. grinding wheels), brake lining to brake shoes, clutch facings, etc. The cement shown in Table 22 is suitable for such diverse jobs as metal-to-metal bonding or brake lining bonding.

**Bonding PVC to Steel, Aluminum Foil, Copper, and Polyurethane.** Nitrile rubber/phenolic adhesives have been utilized to bond PVC to a variety of substrates, including steel,<sup>78-81</sup> aluminum foil,<sup>82</sup> and copper.<sup>83</sup> Contact adhesives have been reported for plasticized PVC.<sup>84-86</sup> A heat-resistant adhesive has

**Table 16. Influence of Resin Content on Adhesion to Steel.**

<i>Rubber-to-Resin Ratio</i>	<i>Resin A, lb/in.</i>	<i>Resin B, lb/in.</i>
10:1	8.3	8.1
4:1	15.6	14.1
1:1	18.3	15.8

Resin A—Monsanto Resin 378 (conditioned 16 hr at 122°F).

Resin B—Durez Resin 11078 (conditioned 2 hr at 121°F).

**Table 17. Physical Properties of Nitrile Rubber and Phenolic Resin Blends<sup>a</sup>.**

<i>Polymer Type</i>	<i>% Acrylonitrile</i>	<i>Tensile at Break (psi)<sup>b</sup></i>
Paracril CV	35	2650
Paracril C	35	2650
Paracril B	29.5	1850
Paracril BJ	29.5	1600
Paracril AJ	23.5	1400

<sup>a</sup>100 parts rubber, 60 parts Durez 12687, 500 parts MEK.<sup>b</sup>films cast on glass, cured 2 hr at 212°F.**Table 18. Adhesive Composition for Printed Circuit Boards.**

Hycar 1072	50
Nicamol PR-1440	30
(Xylene modified phenolic resin)	
Epikote-152	20
Dicyandiamide	0.6
Curazol 2E4MZ	0.2
Aerosil-200	10
in MEK and BuOCH <sub>2</sub> CH <sub>2</sub> OH	

**Table 19. Adhesive Composition for Bonding Steel Plates.**

Nitrile rubber (40% VCN)	100
Stearic acid	1
Zinc oxide	5
Accelerator DM	1
Antioxidant	2
Talc	46
Resol-type phenolic resin	100
Novolak-type phenolic resin	100
Hycar 1312	10
Sulfur	2

**Table 20. Adhesive Composition for Bonding Rubber to Magnesium.**

Hycar 1001CG
Sulfur
Tin oxide
N-phenyl-beta-naphthylamine
Black pigment
2-mercaptobenzothiazole
Durez 12687
Durez 7031A
Hexamethylenetetramine
Chlorobenzene

**Table 21. Nitrile Rubber/Phenolic Resin Tape Formulations.**

Nitrile rubber	100
Phenolic resin	75–200
Zinc oxide	5
Sulfur	1 to 3
Accelerator	0.5 to 1
Antioxidant	0 to 5
Stearic acid	0 to 1
Carbon black	0 to 20
Filler	0 to 100
Plasticizer	0 to 10

Bonding metals to themselves requires heat (20–120 min at 300–400°F) and pressure (50–150 psi).

**Table 22. Structural Adhesive.**

	<i>Parts</i>
Part A	
Phenolic resin (SP-8855)	45.0
MEK/m-chlorobenzene (70/30 by vol.)	90.0
Part B	
Hycar 1001CG polymer	100.0
Carbon black	50.0
Zinc oxide	5.0
Stearic acid	0.5
Sulfur	3.0
Benzothiazyl disulfide (Altax)	1.5
MEK/m-chlorobenzene (70/30 by vol.)	

**Table 23. Adhesives for Leather-to-Leather or Leather-to-Composition Soling.**

<i>Recipe No.</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>
Hycar 1432	20.0	10.0	20.0	10.0
UCAR VYHH	—	10.0	—	5.0
Phenolic resin	10.0	5.0	10.0	5.0
Triphenyl phosphate	—	—	—	2.0
Monochlorobenzene	—	—	90.0	40.0
Methyl ethyl ketone	100.0	75.0	30.0	40.0
Totals	130.0	100.0	150.0	102.0

been used to bond a polyurethane foam to a plasticized PVC sheet.<sup>87</sup> The bonding of PVC, leather substitutes, and shoes has also been reported with nitrile rubber/phenolic adhesives.<sup>88</sup>

**Bonding Leather to Leather, Composition Soling, and PVC.** In the shoe industry, nitrile rubber/phenolic adhesives have been used to bond leather to leather, rubber, and vinyl. A medium high nitrile content rubber (33% VCN) with half as much by weight of a phenolic resin, or this same rubber with half as much or an equal weight of a PVC resin is an effective adhesive for heat activation in the temperature range of 120–130°F. For a higher temperature range adhesive, the use of twice as much of a PVC resin as nitrile rubber is effective. Some suggested combinations<sup>8</sup> which yielded adhesive bonds of 25–40 lb/in. for leather-to-leather, composition soling, or vinyl, are given in Table 23.

**Rubber-to-Rubber Bonding.** Adhesives for rubber-to-rubber bonding have been designed using nitrile rubber/phenolic compositions. Bonding to polar rubbers<sup>89</sup> is especially improved with this type of adhesive. The adhesive composition in Table 24 was designed for splicing cured or uncured nitrile rubber compounds to themselves with heat and slight pressure.<sup>15</sup>

**Miscellaneous Bonding Applications.** Applications have been reported for the use of nitrile rubber/phenolic adhesives in the bonding of wood<sup>90,91</sup> and polyurethane foam<sup>92</sup> to various substrates. Mitsubishi Electric Corp.<sup>93</sup> patented a two-part adhesive composition for Nomex paper (Table 25).

Automotive trim<sup>94,15</sup> and clips<sup>95</sup> have been bonded with nitrile rubber/phenolic adhesives and polyamide has been bonded to rubber<sup>96</sup> and to pavement<sup>97</sup> in a road marking application. Plastic/paper laminates<sup>98</sup> for printing blankets have been prepared. Finally, grit tiles have been bonded to paperboard and other substrates<sup>99</sup> to produce prefabricated tile structures which are stable on application to buildings.

**Sealant Applications.** The repair of engine bodies has been reported using a nitrile rubber/phenolic composition as a sealant.<sup>100</sup> The wing fuel tanks of C130 aircraft have also used nitrile rubber/phenolic materials to seal the tanks.<sup>101</sup> Finally, electrolyte leakage in a sheet battery has been prevented using nitrile rubber/phenolic adhesives.<sup>102</sup>

### Nitrile Rubber/Epoxy Adhesives

Nitrile rubber and epoxy resins have been blended together for use in many adhesive applications. The combination of flexibility and good low temperature properties of nitrile rubber, along with the excellent strength of the

**Table 24. Splice Adhesive.**

Paracril BJ	100
Zinc oxide	15
Aminox	2
EPC carbon black	50
Coumarone indene resin (M.P. 25°C)	25
Durez 12687 (phenolic resin)	20
M-B-T	2
Sulfur	2
	216

Solvent: methyl ethyl ketone.  
Solids content: 20% by weight.

**Table 25. Adhesive Composition for Nomex Paper.**

<i>Part A</i>		<i>Part B</i>	
Hycar 1001CG	100	DEN 438	100
Durez 12687	50	2-methyl-4-ethylimidazole	10
MEK	150	MEK	100

epoxy matrix, has led to adhesives with superior properties in both the laminating and structural area.

**Laminating.** Nitrile rubbers blended with various epoxy resins and activated by suitable amines and/or acidic agents have been employed to bond elastomers, plastics, fabrics, wood, and metals to themselves and each other. Normally good bond strength can be developed at or near room temperature. Any information must be adapted to the substrate being bonded but Table 26 gives a starting formulation. The triethylenetetramine is added as a 50% solution in methyl ethyl ketone just prior to use. Such a cement will cure in 4–24 hours at room temperature and less than 30 minutes at 150°F.

An adhesive consisting of an epoxy resin, a medium high acrylonitrile rubber, and Pb, Cu, Ni, Pd or Co compound fillers was used to bond EPDM vulcanizates.<sup>103</sup> Peel strengths of 22.5 kg/20 mm after a 1 hour at 100°C cure were obtained. Another adhesive composition involving a blend of carboxylated nitrile rubber, epoxy resin and a reactive metal filler has been described for bonding EPDM vulcanizates or EPDM rubber-nitrile or butyl rubber blends.<sup>104</sup>

Other nitrile rubber epoxy adhesives have been described for rubber to rubber and rubber to metal bonds. Liquid carboxylated nitrile materials have been found useful in a number of applications.<sup>105</sup> An adhesive comprised of carboxylated nitrile rubber, epoxy resins, imidazole, or tertiary amine and an organic peroxide has been described<sup>106</sup> for bonding metals, paper, plastics, and inorganic materials.

Combinations of carboxyl-, vinyl-, and amine-terminated liquid nitrile materials in conjunction with an epoxy resin have been described as an excellent adhesive for bonding various fabrics.<sup>107</sup> A formulation for bonding nylon fabric is shown in Table 27.

**Table 26. Low Temperature Curing Nitrile Epoxy Adhesive.**

Hycar 1042	10–50 parts
Epon 820	90–50
Methyl ethyl ketone	80
Trimethylenetetramine	2–20

Foamable adhesive sheets have been produced by blending carboxylated nitrile rubber and epoxy resins, and then adding blowing agents.<sup>108</sup> An epoxy resin containing nitrile rubber has been described to yield increased adhesion of metallic coatings to printing plates.<sup>109</sup>

One of the largest areas of use of nitrile rubber modified epoxy systems is in the printed circuit board area. A number of systems have been described that are composed of carboxyl-containing nitrile rubber such as Hycar 1072 mixed with epoxy resin.<sup>110–117</sup> The low molecular weight functionally terminated nitrile rubbers have also found significant application in this area.<sup>118</sup> Other workers have found useful a system that combines a high molecular weight nitrile rubber with the liquid functionally terminated materials.<sup>119,120</sup> Finally, other references describe the use of non carboxylated nitrile rubbers in circuit board applications.<sup>121,122</sup>

**Structural.** Flexibilized epoxy resins are important commercial structural adhesives.

**Table 27. An Adhesive for Bonding Nylon Fabric.**

Epikote 815	100.0
Bisphenol A	24.0
Hycar 1300X15	223.0
(carboxyl-terminated nitrile)	
Hycar 1300X16	25.0
(amine-terminated nitrile)	

Without the addition of a flexibilizing agent, epoxy resin adhesives have relatively poor characteristics due to the brittle nature of the epoxy matrix.<sup>123</sup> Liquid functionally terminated nitrile rubbers have proved to be an excellent flexibilizing agent for the epoxy resins. It has been theorized that toughening of the epoxy resin occurs by the formation of a rubbery second phase in the epoxy matrix. With nitrile rubbers over 20% acrylonitrile, order of magnitude increases in fracture toughness of the epoxy matrix have been reported.<sup>124,125</sup>

The liquid nitrile rubbers can be reacted into the epoxy matrix in one of two ways. If a carboxyl terminated material is used it is normally adducted or prepolymerized with an epoxy resin prior to formulating. The resulting epoxy adduct is then placed in the epoxy component of the composition. A second method of incorporating liquid nitrile materials would be to use an amine terminated rubber. In this case the material contributes amine reactivity and functions as a part of the hardener system. These materials were primarily developed to form stable admixes with amine containing epoxy hardeners.<sup>126</sup>

CTBN-epoxy adducts have proven useful in both two part room temperature cureable epoxy systems as well as one part heat-curable systems. The inclusion of the nitrile adducts in typical epoxy formulations dramatically increases the T-peel strength and the low temperature/room temperature lap shear strengths while not significantly affecting the elevated temperature lap shear.<sup>127</sup> The amine-terminated liquid nitrile rubbers have been found to improve the toughness of epoxy adhesives when any of the following functional hardeners are employed: amidoamines, polyfunctional aliphatic amines, and fatty polyamides. When formulating a system involving admixing ATBN into the toughener portion, it is important to include the functionality of the ATBN in the stoichiometry of the system.<sup>128</sup>

**Pressure Sensitive.** Mixtures of nitrile rubber and epoxy resin have been described to be useful as pressure sensitive adhesives. One such system combines nitrile rubber, a bisphenol A type epoxy resin methacrylate ester, a product

of maleic anhydride and butadiene, fumaric acid, thioamide, and cumene hydroperoxide. This adhesive was a two part system with the hydroperoxide in one part and the thioamide in the other part.<sup>129</sup>

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### Materials Composition and Source.

Accelerator 808	Butyraldehyde-aniline accelerator; Elastochem Inc.
Accelerator DM	Accelerator; Naftone, Inc.
Acrysol GS	Sodium polyacrylate; Rohm and Haas
Aerosil 200	Colloidal silicas; Degussa Inc.
AgeRite Resin D	Polymerized 1,2-dihydro-2,2,4-trimethylquinoline; R. T. Vanderbilt
Altax	Benzothiazyl disulfide; R. T. Vanderbilt
Aminox	Diphenylamine acetone reaction product, Uniroyal Chemical
Butyl Eight	Activated dithiocarbamate; R. T. Vanderbilt
BRT-7	Refined coal tar; Allied Chemicals Corporation
Carbopol 934	Poly(acrylic acid); BFGoodrich, Speciality Polymers and Chemicals Division
Chemigum	Nitrile rubbers; Goodyear Tire and Rubber Co.
Chlorowax 40	Chlorinated paraffin; Diamond Shamrock
Dixie Clay	Hydrate aluminum silicate; R. T. Vanderbilt
Durez	Phenolic resins; Occidental Chemical
EPC	Carbon black; J. M. Huber Corp
Epikote 152	Epoxy resin; Shell Chemical Co.
Epikote 815	Epoxy resin; Shell Chemical Co.
Epon 820	Epoxy resin; Shell Chemical Co.
Flexricin P-4	Plasticizer; Baker Castor Oil Co.
Geon 450x20	PVC latex; BFGoodrich, Elastomers and Latex Division
HiSil	Precipitated hydrated amorphous silica; PPG Industries Inc.
Hycar	Nitrile rubbers; BFGoodrich, Elastomers and Latex Division
Litharge	Lead oxide; Eagle Pitcher Industries, Chemical Division
MBT	2-Mercaptobenzothiazole; Uniroyal Chemical Co.
Monsanto Resin 378	Phenolic resin; Monsanto Chemical Co.
Nicamol PR-1440	Xylene modified phenolic resin; Mitsubishi Gas Kagu KK
Paracril	Nitrile rubbers; Uniroyal Chemical (Avery International)
Paraplex G-30	Polymeric plasticizer; C. P. Hall
Picconol A600E	Aromatic resin emulsion; Hercules Inc.

**Materials Composition and Source (*Continued*)**

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SP-8855	Phenolic resin; Schenectady Chemicals
Stafflex QXMA	Barium stabilizer; Reichold Chemical
Sterling S	Carbon black
Titanox	Titanium dioxide; Titanium Pigment Corp.
Turpol 1093	Polymeric plasticizer; Irvington Chemical Division of 3M
Ucar VYHH	Vinyl chloride-vinyl acetate copolymer; Union Carbide Corporation
Unads	Tetramethylthiuram monosulfide; R. T. Vanderbilt Co.
Vinsol	Thermoplastic Resin; Hercules Inc.

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# Styrene-Butadiene Rubber Adhesives

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## INTRODUCTION

### Perspective

Adhesives have long represented a market, albeit relatively small, for styrene-butadiene rubbers. The original commercial SBR was used successfully in this application and today all of the SBRs, solution types as well as hot and cold emulsion types, are used in a variety of adhesive compositions. They are used by adhesive formulators as latexes or as solid rubbers.

In 1985 the consumption of SBR in the United States was about 1.8 billion pounds. Of this, about 64% was used in the manufacture of tires and related products. Although SBR is significant among the polymers used in adhesives, less than 1% of the total SBR consumption was accounted for by this end use.

### History of SBR

Styrene-butadiene rubber first established its industrial importance during World War II, when it played a key role as a substitute for natural rubber which was in short supply. The original styrene-butadiene rubber manufac-

tured in North America was produced in several plants under government programs and was known as GR-S (government rubber—styrene). After the war the production facilities were sold to private enterprise and the product became known as SBR.

The wartime SBR was essentially a single grade multi-purpose rubber. Relative to natural rubber it was deficient in tensile strength, elongation, resilience, hot tear, and hysteresis. On the other hand it represented an advance over natural rubber in such key characteristics as abrasion resistance, aging and product uniformity.

Following World War II the focus on SBR turned to development of specific products demonstrating improvement in selected properties over natural rubber as well as the original SBR. The first such development was the emulsion polymerization of styrene and butadiene at low temperature in the presence of a redox catalyst system. The product from this type of process represented a marked improvement over natural rubber in tread stocks for passenger car tires. Subsequently, application of organolithium catalysis permitted development of solution-polymerized SBRs that offered improvements over emulsion SBR in curing rate

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\*Formerly with Polysar

and abrasion resistance, although the short styrene blocks characteristic of these polymers adversely affected resilience in tire applications.

### Manufacture of SBR

The process of manufacturing styrene-butadiene rubber consists of three distinct steps: polymerization, monomer recovery, and finishing. The basic characteristics of the polymer, which are outlined below, are determined in the polymerization step, and the product form, whether latex or dry rubber, oil extended or not, is a function of the finishing process.

### Basic Chemistry of SBR

SBRs are produced by addition copolymerization of styrene and butadiene monomers in either an emulsion or a solution polymerization process. The ratio of styrene to butadiene controls the glass transition temperature ( $T_g$ ) of the copolymer and thus the stiffness of the elastomer. The higher the styrene content, the higher the  $T_g$  and stiffness. Polymers can be made over the whole range of  $T_g$  from about  $-80^\circ\text{C}$  for polybutadiene to about  $+100^\circ\text{C}$  for polystyrene.

Because butadiene has two double bonds, two modes of addition can take place: 1,2 and 1,4. The 1,2 addition yields a pendent vinyl group on the growing chain, which increases  $T_g$ . The 1,4 addition can occur with the polymer chains *cis* or *trans* to the residual in-chain double bond. The more regular *trans* configuration leads to better cured tensile properties.

The microstructure of the elastomers can be controlled by the manufacturing process. In emulsion polymerization, which is a free radical process, the proportion of *cis* and *trans* structures can be varied by changing the temperature of polymerization. High *trans* (about 70% of polybutadiene) results at low temperatures (about  $-10^\circ\text{C}$ ) and higher *cis* at high temperatures, where the *trans* content can drop to about 50% (at about  $100^\circ\text{C}$ ). The pendent vinyl content remains fairly constant at about 20%. The presence of styrene in the system has little effect on the relative proportions of the different butadiene structures in the polymer.

In solution SBR the pendent vinyl content can be varied from 10 to 90% by choosing a sol-

vent system of an appropriate polarity or by complexing the catalyst with ether.

A random solution SBR will have almost equal amounts of *cis* and *trans* configuration, but this can be varied. For example, a change in catalyst composition can increase the *trans* content to 70%.

The double bond in butadiene-derived macromolecules can be subject to attack by the free radicals in the emulsion polymerization reaction. Growing chain radicals can propagate through the double bond of an already formed chain so that two chains become joined or crosslinked. If this process is allowed to continue, more and more chains become linked together until all molecules become linked to all other molecules and the molecular weight approaches infinity. Such structures are called *gels*. The amount of crosslinking and the gel content of the polymer can be controlled in emulsion polymers by the polymerization temperature, the extent of conversion of monomer to polymer, and the use of chain transfer agents (so-called *modifiers*). High reaction temperatures enhance the crosslinking reaction.

Initiation of the solution SBR reaction is very rapid in comparison with chain propagation, and because there is little termination or chain transfer, a very narrow molecular weight distribution may be produced. Broadening can be achieved by use of polar additives and continuous rather than batch polymerization processes. The molecular weight can be influenced by the monomer-to-catalyst ratio. Branching and crosslinking can be encouraged by the addition of a third monomer or branching agent, such as divinyl benzene or tin tetrachloride.

## SBR LATEXES IN ADHESIVES

### General

An important feature of latexes is that they are sold and used as such. This means that in most applications the consumer does not normally have the opportunity to modify latex properties before use. In dry rubber systems the molecular weight of the polymer is modified by the consumer to his specific needs by milling, mastication, etc. Hence a few grades cover a multitude of applications. This flexibility generally is not possible with latex. The desired

properties in the final end use must be built in by the latex manufacturer during polymerization. Much proliferation of latex grades has resulted compared with dry rubber grades and a low level of standardization prevails among manufacturers, particularly in functional styrene-butadiene grades.

### Classification

Three broad classes of SBR latex are available in the market place.

1. Cold-polymerized, high-solids latex, often called *high solids* or *cold latex*.
2. Hot-polymerized, medium-solids latex, often called *medium solids* or *hot latex*.
3. Hot-polymerized, medium solids latex produced in the presence of small amounts of an unsaturated carboxylic acid monomer, and hence usually referred to as *carboxylated latex*.

The characteristics of the three classes are discussed below.

**Cold Latexes.** These latexes are normally produced by emulsion polymerization at temperatures below 15°C, although higher temperatures can sometimes be used. Polymerization at subzero temperatures is feasible as well in the presence of a suitable freezing point depressant.

These latexes usually contain polymers with styrene content in the range 20–35%, the remainder of the polymer being made up of the butadiene component. They are usually polymerized with a redox initiator system (on a batch or continuous basis), and because of the low polymerization temperature are characterized by fairly linear, high-molecular-weight polymer content. The gel content is controlled by short-stopping the reaction at a relatively low (50–75%) conversion level. A typical Mooney viscosity of the rubber component of such a latex would be about 120 (ML 1 + 4' @ 100°C).

The surfactant system is usually of the natural soap type, i.e., either rosin or more often fatty acid. The latexes, at this stage, are of small particle size (less than 1000 Å) and of low to medium solids content. Some latexes are sold in this state, but most are put through an

agglomeration process to increase the particle size and broaden the particle size distribution so that they can be concentrated to the usual commercial level of about 60–70% solids. Agglomeration can be achieved by controlled freezing, high shear, or use of chemical additives.

Because a natural soap type of surfactant is used in the polymerization these latexes are only stable at pH above 8.5–9.0 and are sold in the pH range 10–11 to ensure stability. In general they are not very stable to added multivalent metal salts, although more so than natural rubber latexes, and care must be exercised in compounding.

Films made from these latexes show high extensibility and low modulus. The best physical properties are only realized when a cure system such as a conventional sulfur/accelerator combination is used.

**Medium-Solids Hot Latexes.** These latexes are manufactured by emulsion polymerization at temperatures above 30°C. The styrene content of the polymer is normally about 45% and the remainder is butadiene, although styrene content can be anywhere in the 0–100% range. These products are the direct descendants of the original GR-S polymers.

Because of the relatively high polymerization temperature the polymer molecules are much less linear than cold polymers and they have a lower primary molecular weight because modifiers are used to attempt to control gel content. The gel content is potentially higher in grades which are not short-stopped at relatively low conversion. Typical Mooney viscosities lie in the range 45–80 (ML 1 + 4' @ 100°C) but products with much higher values are available. Films from this type of polymer tend to have lower elongation and higher modulus than their cold counterparts. Again, for the best properties a cure system may be necessary.

Aside from a lower solids content of 40–50%, medium-solids latexes are similar to cold latexes in most other respects. The surfactant systems are either fatty or rosin acids, with the latter probably more common in this instance. The latexes are generally of somewhat larger particle size than unagglomerated cold latexes and the stability of the two classes is similar.

A special subclass of this type of latex is the vinyl pyridine (VP) group. Members of this group contain up to 30% vinyl pyridine as termonomer and 15–25% styrene. Cold polymerized analogs are also available.

**Carboxylated Latexes.** Carboxylated latexes are produced over a wide range of styrene contents and incorporate at least one type of unsaturated carboxylic acid in quantities up to about 10% by weight of total monomers. Other functional monomers can also be used either instead of or in conjunction with acidic monomers in order to modify such properties as stability and crosslinkability. Such modified products generally are classed as carboxylated latexes though they will sometimes be termed self-crosslinking or heat-reactive, as well.

Carboxylated latexes usually are made by hot polymerization processes characterized by high conversion. They tend to have high gel content and very high Mooney viscosities. As a consequence the Mooney test is not often used to characterize them.

Because these materials are polymerized at acid *pH* to ensure incorporation of the acidic monomer, synthetic surfactants such as dodecylbenzene sulfonic acid are used. Normally the *pH* of the system is raised with alkali at the end of reaction and the product is sold in the range of *pH* 6–10 depending on manufacturing process and grade.

The chemical and mechanical stability of this class of latex usually is much greater than that of the other two classes.

Films of carboxylated latexes vary considerably in properties but generally are of lower elongation and higher modulus than their non-carboxylated counterparts. Cure systems are not normally necessary but may be used in some special applications for the development of specific properties. Conventional sulfur vulcanization can be used in some cases (lower styrene, lower gel) but more often materials that react with the functional groups are used (e.g., zinc oxide or melamine formaldehyde resins).

### Benefits of SBR Latexes

Latexes offer several advantages over other elastomer systems. They represent high-solids

dispersions of rubber particles in water, the viscosity and rheology of which are in general independent of the polymer properties, unlike solutions. The vehicle (water) is nontoxic, nonflammable, and inexpensive. They offer a wide range of molecular weight and glass transition temperatures. Particularly with the lower styrene (lower  $T_g$ ) polymers one has the advantage of a very rubbery elastomer with low thermoplasticity when compared to most other polymers available in emulsion form. The gel portion of the polymers represents internal crosslinks which are often sufficient to give good strength and creep resistance properties without recourse to further curing.

### Compounding Ingredients

The major ingredients for rubber based adhesives in addition to the elastomer are given below:

1. Tackifiers.
2. Plasticizers/oils
3. Solvents.
4. Fillers.
5. Curing agents (not required in all instances).
6. Stabilizers:
  - light, oxidation.
  - colloidal.
7. Thickeners.
8. Miscellaneous.

For latex systems, all these materials must be water dispersed, water dispersable, or water soluble.

**Tackifiers.** Although SBRs can be produced with tack, the physical properties of such polymers usually do not fully satisfy the application requirements. For this reason tackifying resins are normally incorporated into adhesives based on SBRs. These resins improve the kinetics of wetting and increase the overall  $T_g$  of the adhesive composition. Typical tackifiers for SBR are rosin-based materials, aromatic-containing petroleum hydrocarbon resins, alpha-pinene, coumarone-indene, and some phenolic resins.

**Plasticizers/Oils.** Oils and plasticizers are added to adhesive compositions for a number

of reasons. They can be used to soften the elastomer, improve the compatibility between the polymer and other additives, act as a vehicle for introducing other additives, or act solely as an extender to reduce cost. They also change the wetting characteristics of the elastomer and its film-forming ability. Typical examples are organic phosphates, phthalate esters, and aromatic hydrocarbon oils.

**Solvents.** Solvents are added for much the same reasons as oils and plasticizers. Additionally they may interact with the substrate, e.g., by partially dissolving it. Because they can be volatile they may also be used as fugitive plasticizers to modify the drying and coalescence behavior of the adhesive.

Water soluble solvents such as alcohols can easily destabilize the latex and care must be exercised in their use. As aliphatic hydrocarbon solvents tend not to be compatible with SBR polymers, aromatic or polar solvents are preferred.

In view of the current trend to replacement of solvent-based systems by latexes in many adhesives it is desirable to limit the use of solvents so that the advantages of water-based systems can be fully exploited.

**Fillers.** Fillers are added to latexes to reduce materials cost, increase volume or weight, and/or modify properties. The major modifications which can be achieved with filler are changes of color or opacity, changes of density, increase of solids content, change of rheology, and increase in stiffness or modulus of the adhesive.

Often fillers are added to latexes as separate slurries, particularly in the case of noncarboxylated latexes, though preaddition of wetting or dispersing agents and surfactants can promote distribution of a dry filler. Carboxylated latexes have the advantage of being tolerant of dry filler additions.

Typical fillers in latex systems are calcium carbonate in a variety of forms, clays and silicas. Materials such as barytes are employed to increase density; titanium dioxide, carbon black, or iron oxides are used to change color.

The main guideline in compounding fillers into latex systems is to be sure to add sufficient

compatible surfactant and/or wetting agent to satisfy the total surface area needs of the system, particularly if the fillers are of small particle size.

**Curing Agents.** Although SBR latexes often do not require use of curing agents in the normal sense, a number of cure systems are available. For noncarboxylated latex compositions, conventional sulfur systems may be used where external heat can be applied. Otherwise phenolic cures may be used or self crosslinking resins may be blended into the formulation.

While carboxylated latexes are widely accepted as not needing a cure system, those described above for SBRs are applicable, as are melamine formaldehyde or other formaldehyde condensates. Multivalent metal compounds may also be used with carboxylated systems; the most common of these is zinc oxide, but other materials such as zirconium ammonium carbonate may also be used. Some of these types of materials have the advantage that they are effective at room temperature. Some functional SBR latexes have their own cure system built into the polymer and are often referred to as *self-crosslinking*, or as *heat-reactive* in instances where heat is involved in the curing process.

**Stabilizers.** With polymers, the term stabilizers normally refers to materials which provide UV light and thermal oxidative protection. However, with latex, two other needs arise—resistance to bacterial attack, and colloidal stability. The latter will be dealt with in more detail in the following section.

Latexes, as sold, will normally contain a bactericide. However when compounds are produced from these latexes the bactericide is diluted and other potentially biodegradable materials are included. Hence it is prudent to add bactericidal agents to water based adhesive compounds.

Most commercial latexes contain an antioxidant, although some, such as the cold, high-solids types, usually do not. A check with the latex manufacturer is advisable to establish whether his product contains sufficient antioxidant to provide adequate protection against thermal oxidative degradation for the final ad-



hesive compound. Hindered phenols are the most commonly used nonstaining antioxidants.

Under some end-use conditions, where an adhesive may be exposed to UV light, addition of suitable UV absorbers and stabilizers might be considered.

**Colloid Stabilizers.** In many water-based systems it is necessary to add colloid stabilizers for specific purposes. One can distinguish three classes:

1. *Surfactants.* Common surface active agents may be added to enhance the colloid stability against mechanical and chemical stress, to help to disperse other particulate materials (e.g., fillers or curing agents), to aid in wetting substrates, or to enhance foaming. Dodecylbenzene sulfonates and potassium oleate are typical of this class.
2. *Wetting Agents.* These materials are used primarily to wet particulate materials and to aid colloidal stability without foaming. The naphthalene sulfonate/formaldehyde condensates are examples of this class.
3. *Sequestrants.* These materials are added to protect the latex from soluble multivalent ions through complex formation. A common agent is ethylenediaminetetraacetic acid (EDTA). Some materials can also assist in dispersion of inorganic materials in latex as well as act as sequestrants. Typical of this class is tetrasodium pyrophosphate (TSPP).

**Thickeners.** Because the rheology of the latex aqueous phase is largely independent of the nature of the dispersed phase, semi-independent control of rheology is feasible. Hence viscosity modifiers or thickeners become important compounding ingredients. Examples of such materials include natural products such as gums, starch, proteins, and alginates; synthetic materials such as polyacrylates; and modified natural materials such as carboxymethyl cellulose. Thickeners can also act to control water loss both to substrates and during drying.

**Miscellaneous.** A number of other materials may be added for special purposes. One

which is often necessary is an antifoam. The latter is usually of one of three basic types: silicone, mineral oil, or surfactant. The latter two are preferred for temporary or short-term effects; silicones are preferred for more permanent action but with the danger of defects in the films such as fish-eyes.

## Major Applications

**General.** SBR latex adhesives are normally used in applications where there will be relatively low stress but where durability, flexibility, and a measure of shock resistance are required. They have relatively low surface free energy and are therefore useful in general purpose adhesives which have to bond to a variety of substrates. When properly compounded they have good resistance to environmental deterioration, though they will not retain good color when exposed to ultraviolet light.

**Tufted Carpet Backing.** The major application of SBR latex is as an adhesive in the tufted carpet industry. Carboxylated SBR latex compounded with calcium carbonate filler is used as the adhesive to secure the tufts in the backing and as an adhesive for so-called secondary backings.

For anchoring tufts alone, either as a unitary backing or more commonly as a so-called tie coat prior to foam backing, the latex is compounded with up to 500 phr filler (typically ground limestone) and applied to the raw tufted carpet by means of lick roll and doctor blade. The adhesive is dried by infrared heaters or by passage through a hot-air circulating oven. For secondary backing a layer of cloth is wet-laminated to the back of the carpet before drying. Traditionally the cloth was woven jute (burlap) but is now more commonly woven or nonwoven polypropylene or polyester. A typical adhesive compound is described in Table 1.

**Paper Coatings.** Carboxylated SBR latexes are also important either alone or in combination with other material such as starch or casein as an adhesive or binder for clay coatings for printing papers.

**Nonwovens.** Carboxylated SBR is the primary adhesive or binder in a number of non-

**Table 1. Carpet Secondary Backing Adhesive.**

	<i>phr (dry)</i>
Carboxylated SBR latex (55% styrene)	100
Sequestrant (e.g., tetrasodium pyrophosphate)	0.3
Ground limestone	350
Water to 78% total solids content (TSC)	
Polyacrylate thickener to 15,000 mPa·s	

woven cloths, principally those used for wipes, diaper cover stocks, and garment interlinings. Typically the latex is self-curing or compounded with a curing agent (e.g., melamine-formaldehyde resin) and applied by spraying, by saturation on a foulard, or by print bonding.

High-styrene latexes are used in the shoe industry as saturants for woven or nonwoven shoe-stiffening fabrics. The dried, saturated sheet material is molded and laminated to other materials in one operation. Sometimes an external adhesive is used, but the dried latex can itself act as the adhesive either by activation with a solvent such as toluene or by heating.

**Doubling Adhesives.** SBR latexes are used for a variety of laminating or doubling operations. There are two basic processes, one where the two materials are combined with the adhesive in the wet state and the other where the adhesive is dried before the materials are brought together. In the latter case both materials to be laminated are normally coated whereas in the former case only one substrate may be coated.

For the wet process, latex is used alone or with filler and thickened to a viscosity appropriate to the process. Traditionally many of these operations were carried out using hot noncarboxylated types with or without sulfur vulcanization, but carboxylated latexes are increasing in importance.

In the dry process, latex is normally compounded with tackifying resins to create sufficient tack for the dry combining operation.

Typical materials which can be combined are woven textiles, paper, paper to metal foil, plastic films, plastic film to paper, leather, and leather to cloth. This type of process is common in the textile industry, the paper converting and packaging industry, the automotive

**Table 2. Adhesive for Lamination of Aluminum Foil to Kraft Paper.**

Carboxylated SBR latex (42% styrene)	100 phr (dry)
Sodium polyacrylate thickener to 2,000–3,000 mPa·s	
Water to a total solids content of 50%	

industry and its suppliers, and the shoe industry. A typical formulation is shown in Table 2.

**Construction Adhesives.** Much SBR latex is used in adhesives directed to the construction industry. Wall tile and vinyl floor tile adhesives are typical examples (see Table 3 for formulation). SBR latexes, both carboxylated and noncarboxylated types, are often added to cement mixtures to improve adhesion in repair work. Sealants and caulks can be based on SBR.

**Tire Cord Dip.** Tire cord adhesives is another important outlet for latexes. A basic formulation is given in Table 4. The latex is mainly a vinyl pyridine (VP) type. Depending on the fiber to be bonded, the VP latex can be diluted with hot SBR or nonagglomerated cold SBR latex. The dilution depends on the difficulty of bonding the different fibers. Rayon was easy to bond to the carcass and did not require VP latex. Substitution of rayon by nylon and polyester tire cords necessitated the development and use of VP latex.

**Table 3. Typical Vinyl Flooring Adhesive.**

	<i>phr (dry)</i>
Part A:	
25° S.P. hydrocarbon resin	212.5
Mineral spirits	37.5
Dioctyl phthalate	12.5
Methanol	12.5
Nonionic surfactant	7.5
Clay	50.0
Part B:	
High-solids SBR latex	100
Phosphate stabilizer	0.5
Potassium hydroxide	0.25
Defoamer	0.10
Water to 60% total solids content	

A and B are mixed under good agitation. Sodium polyacrylate is used to adjust viscosity to 50,000–60,000 mPa·s.

Table 4. Typical Tire Cord Dip.

	<i>parts by weight</i>	
	<i>dry</i>	<i>wet</i>
Water	—	25.8
Resorcinol	9.4	9.4
Formaldehyde	5.1	13.8
Caustic soda	0.7	7.0
Latex	84.8	212.0
	100.0	500.0

**Pressure-Sensitive Adhesives.** A relatively new application area for SBR latexes is that of the pressure sensitive adhesives. Traditional solvent-based adhesives are being replaced by hot melt and water-based systems. SBR latex is being used increasingly in a number of specific areas. Typical formulations are shown in Tables 5–7.

Table 5. Pressure-Sensitive Adhesive for Paper Labels.

	<i>phr (dry)</i>
Carboxylated SBR latex (25% styrene)	100
85° S.P. rosin ester resin	75
Sodium polyacrylate thickener to 700–800 mPa·s.	
Total solids content 50%	

Table 6. Pressure-Sensitive Adhesive for Masking Tape.

	<i>phr (dry)</i>
Carboxylated SBR latex (25% styrene)	50
Low-ammonia natural latex	50
85° S.P. rosin ester resin	20
85° S.P. hydrocarbon resin	60
Antioxidant	2.0
Titanium dioxide	1.0
Sodium polyacrylate thickener to 600–800 mPa·s	
Total solids content 50%	

Table 7. Pressure-Sensitive Adhesive for Biaxilly Oriented Polypropylene Tape.

	<i>phr (dry)</i>
Carboxylated SBR latex (25% styrene)	100
85° S.P. rosin ester resin	40
Hexamethoxymethyl melamine	3
Sodium polyacrylate thickener to 400–600 mPa·s	
Total solids content 50%	

SBR (SOLID) IN ADHESIVES

General

Solid SBRs offer unique value to the marketplace in spite of being thought of, originally, as a mediocre substitute for natural rubber. They are often preferred to natural rubber because of performance advantages in areas such as thermal oxidative stability, abrasion resistance and processability, that have resulted from extensive development activity. In addition they usually have a manufacturing cost advantage over natural rubber.

Emulsion SBRs have been standardized to a large degree among manufacturers, with the IISRP\* offering a standard numbering scheme to identify the different manufacturers' grades (see Table 8). Solution SBRs, however, have only recently begun to proliferate and manufacturers' product lines cannot be compared readily.

Classification

Solid SBRs are usually grouped in four major families by method of production, which determines some broad differences in properties.

**Emulsion SBR.** Two of the four families, cold and hot emulsion rubbers, are made by the polymerization processes described earlier for

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Table 8. IISRP Numbering System.

<i>Series</i>	<i>SBR</i>
1000	Hot-emulsion polymers
1100	Hot-emulsion black masterbatch with 14 or less parts per hundred SBR
1200	Solution SBR
1500	Cold-emulsion polymers
1600	Cold-emulsion black masterbatch with 14 or less parts of oil per hundred SBR
1700	Cold-emulsion oil masterbatch
1800	Cold oil black masterbatch with more than 14 parts of oil per hundred SBR
1900	Miscellaneous dry polymer masterbatches

latex products. The solid rubber is isolated from the latex by a coagulation process. Hot SBRs are used more frequently than cold SBRs in adhesive formulations.

**Solution SBR.** The manufacturing process for solution SBR generates a product essentially free of such nonrubber polymer ingredients as the surfactants required in the emulsion process. These rubbers are gel-free and have a narrower molecular weight distribution than their emulsion-polymerized counterparts. This narrow distribution makes it more difficult to modify the polymer viscosity by milling.

#### **Oil and Carbon Black Masterbatches.**

These grades, geared to the tire and retread industries, are high molecular weight, high viscosity, raw polymers, plasticized for easy processing with extender oils (15–65 phr) and/or mixed with carbon black (40–100 phr) in the SBR production process. Better dispersions than those obtained by conventional mixing are generated in this manner.

### **Compounding Ingredients**

Compounding ingredients for dry rubber are similar to those used with latex except that they reflect the absence of the aqueous phase. Thus latex water-phase-type ingredients such as thickeners are not needed but the ingredients that are used must be soluble or dispersible in the solvents used to dissolve the rubber.

### **Major Applications**

**General.** Solid SBRs play an important role in the adhesives industry. They are used in many general purpose and specialty applications, including general purpose construction adhesives, tape adhesives, and pressure-sensitive adhesives.

Solid SBRs find their major adhesive role in solvent-based adhesives, with small amounts also used in mastics and hot melts. Most SBRs are easily dissolved in aliphatic, aromatic, and chlorinated hydrocarbons. Highly crosslinked grades, however, may swell or form a gel-like solution, and high bound-styrene copolymers

do not dissolve in low-boiling aliphatic hydrocarbons (pentane, hexane).

SBR adhesives provide good flexibility and water resistance and offer better aging characteristics than natural rubber or natural rubber reclaim. They are not generally used for high sustained load or where aging characteristics are critical.

**Pressure-Sensitive Adhesives.** SBR is widely used in pressure-sensitive adhesives for such applications as labels, surgical tape, masking, protective wrapping, and splicing. A formulation for a pressure-sensitive adhesive with stable medium viscosity and good peel strength is shown in Table 9.

Compositions of this type are usually coated to tape-backings (paper, plastic, cellophane, cloth). The coated substrate should adhere tenaciously on application of light pressure, yet allow a clean release.

**Sprayable Adhesives.** Sprayable adhesives are widely used in tire building and retreading, and for application to other substrates such as paper, wood, plastic, and cloth. The use of crosslinked hot SBR helps produce discrete particles when the adhesive is sprayed, and controls webbing of the adhesive on application. When crosslinked grades are used for this purpose in conjunction with regular SBR, the polymers should be milled separately and then dissolved together to create a solvent blend. This procedure will make the most of the crosslinked grade's contribution to the blend's rheological properties.

**Table 9. Pressure-Sensitive Adhesive.**

<i>Compound</i>	<i>phr</i>
SBR 1570	50
SBR 1509	50
Antioxidant	1.9
Glycerol Ester of Hydrogenated Rosin	131
Petroleum Hydrocarbon (b.p. 67–87°C)	<u>525</u>
Total	757.9
Viscosity (mPa·s) Brookfield LTV, Sp. #3, 12 rpm	
after 48 hours	1600
after one month	1580

**Table 10. Spray Grade Cement.**

<i>Compound</i>	<i>phr</i>
SBR 1006	50
SBR 1009	50
Natural rosin	70
Dimerized rosin	30
Antioxidant	2
Petroleum hydrocarbon (b.p. 67–87°C)	800
Total	1002
Viscosity (mPa·s) Brookfield LVT, Sp. #2, 12 rpm	
after 48 hours	450
after one month	400

The formulation in Table 10 shows considerable improvement in spraying properties compared to compounds based on regular SBR.

**Laminating Adhesive.** Laminating adhesives are used to combine two or more plies of materials to form a new composite. One-way

**Table 11. Low-Temperature-Curing Laminating Adhesive.**

<i>Mill Compound</i>	<i>phr</i>
SBR 1570	50
SBR 1516	50
Hard Clay	50
Titanium dioxide	10
Sulfur	3
Zinc oxide	5
Stearic acid	1
Diethylene glycol	1
Total	170

<i>Adhesive Compound</i>	<i>parts by weight</i>
Mill compound	25.0
Pentaerythritol ester of dimerized rosin	7.0
Antioxidant	0.2
Petroleum hydrocarbon (b.p. 67–87°C)	68.0
Total	100.2
Viscosity (mPa·s) Brookfield LVT, Sp. #3, 12 rpm	
after 48 hours	2100
after one month	2400
<i>Catalyst</i>	<i>parts by weight</i>
Activated dithiocarbamate	10
1,1,1-Trichloroethane (inhibited)	90
Total	100

[T-Peel strength for 100 pts adhesive, 10 pts catalyst, Cotton Duck No. 8.

after 1 week	14 lb/in. (2.5 kg/cm)
after 1 month	19 lb/in. (3.4 kg/cm)]

wet binding is feasible if at least one of the surfaces is porous. Otherwise, both surfaces are coated and bonding pressure is applied after the solvent has evaporated. The cement can be sprayed on or applied by knife or roller. A typical low-temperature-curing adhesive is shown in Table 11. The catalyst is added just prior to application and the mixture cures within one week.

**Fabric-to-Metal Adhesive.** The formulation in Table 12 is designed for good heat resistance which is often required in automotive applications. One-way wet binding is feasible if the fabric is permeable.

**Expanded Polystyrene Cement.** In the case of adhesives for bonding to expanded polystyrene, the choice of solvents is critical. Expanded polystyrene cells will collapse when attacked by aromatic hydrocarbons, ketones or esters. Even the low aromatic concentrations found in textile spirits, for example, will cause cell collapse as the material ages. The chosen solvent must be free of harmful contaminants, and used with a polymer which will form a stable solution of acceptable viscosity. The formulation in Table 13 produces good adhesion to metal, wood, and concrete. It is applied to both surfaces and dried before bonding under hand pressure.

**Ceramic Tile Cement.** Organic adhesives are popular for bonding ceramic tile to plaster, concrete and plywood in interior installations.

**Table 12. Fabric-to-Metal Adhesives.**

<i>Compound</i>	<i>phr</i>
SBR 1006	100
Natural rosin	33
Polymerized rosin	85
Pentaerythritol ester of dimerized rosin	33
Zinc oxide	10
Antioxidant	2
Petroleum hydrocarbon (b.p. 67–87°C)	414
Total	677

Viscosity (mPa·s) Brookfield LVT, Sp. #3, 12 rpm

after 48 hours	2750
after one month	3000

**Table 13. Expanded Polystyrene Cement.**

<i>Compound</i>	<i>phr</i>
SBR 1570	100
Dimerized rosin	106
Hydrogenated rosin	45
Antioxidant	2.7
Hexane	654
Total	907.7
Viscosity (mPa·s) Brookfield LVT, Sp. #3, 12 rpm	
after 48 hours	1575
after one month	1500

These adhesives are masticlike solvent compositions which develop final bond strength

**Table 14. Ceramic Tile Cement.**

<i>Compound</i>	<i>phr</i>
SBR 1018	18.6
SBR 1009	81.4
Petroleum hydrocarbon (b.p. 116–136°C)	407
Calcium carbonate	151
Hard clay	232
Antioxidant	2.3
Polymerized rosin	244
Total	1136.3

gradually as the solvent dissipates from the glue line. The open time can be altered by using lower- or higher-boiling fractions of petroleum hydrocarbons. A typical formulation is given in Table 14.

### Suppliers of Styrene-Butadiene Rubbers.

<i>Supplier</i>	<i>SBR Type</i>	<i>Trademark</i>
American Synthetic Rubber Corporation P.O. Box 32960 Louisville, KY 40232	Series 1000, 1500, 1700, 1900 and latexes	Amsyn ASRC Flosbrene Flostex
Copolymer Rubber and Chemical Corporation P.O. Box 2591 Baton Rouge, LA 70821	Series 1500, 1600, 1700 and 1800	Copo Carbomix
DiversiTech General Chemical/Plastics Division P.O. Box 951 Akron, OH 44329	Series 1500, 1600, 1700, 1800 and latexes	Gentro Gentro-Jet Gen-Tac Gen-Flo
Dow Chemical USA Coatings and Resins Department Midland, MI 48674	Latexes	Dow
Firestone Synthetic Rubber Company 381 W. Wilbeth Road Akron, OH 44301	Series 1200	Duradene Steron
BF Goodrich Ameripol Tire Division 500 S. Main St. Akron, OH 44318	Series 1000, 1500, 1600, 1700, 1800, 1900 and latexes	Ameripol Good-Rite
Goodyear Tire and Rubber Company Akron, OH 44316	Series 1000, 1200, 1600, 1700, 1800, 1900 and latexes	Pliolite Plioflex
W.R. Grace and Company Organic Chemicals Division 55 Hayden Ave. Lexington, MA 02173	Latexes	Darex
BASF Corporation Fibres Division 3805 Amnicola Highway Chattanooga, TN 37046	Latexes	Butofan Butonal Styrofan Styronal

**Suppliers of Styrene-Butadiene Rubbers ( *Continued* )**

<i>Supplier</i>	<i>SBR Type</i>	<i>Trademark</i>
Polysar Limited 1265 Vidal Street S. Samia, Ontario N7T 7M2	Series 1000	Polysar S1018
Reichhold Chemicals Incorporated P.O. Box Drawer K Dover, DE 19901	Series 1000 and latexes	Tylac
Shell Chemical Company One Shell Plaza P.O. Box 2463 Houston, TX 77001	Latexes	Kraton
SYNPOL (Inc.) P.O. Box 667 Port Neches, TX 77651	Series 1000, 1500, 1600, 1700, 1800 and 1900	SYNPOL
Uniroyal Inc. Chemical Group Middlebury, CT 06749	Series 1900	
Unocal Corporation Chemicals Division 1900 East Golf Road Schaumburg, IL 60195	Latexes	

# Thermoplastic Rubber (A-B-A Block Copolymers) in Adhesives

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## WHAT IS THERMOPLASTIC RUBBER?

Thermoplastic rubber is truly a useful and versatile class of polymer. It has the solubility and thermoplasticity of polystyrene, while at ambient temperatures it has the toughness and resilience of vulcanized natural rubber or polybutadiene. This characteristic results from its unique molecular structure. Visualize the simplest thermoplastic rubber molecule: a rubbery midblock with two plastic endblocks. This situation is pictured schematically in Fig. 1 where the diamonds represent monomer units in the plastic endblocks and the circles represent monomer units in the rubbery midblock. Such a molecule is called a block copolymer.

Patent and scientific literature<sup>1-4</sup> describes numerous molecular variations: the structure pictured in Fig. 1 (A-B-A), more than two monomers (A-B-C), branched or radial configurations

A  
|  
(A-B-A), repeating segments

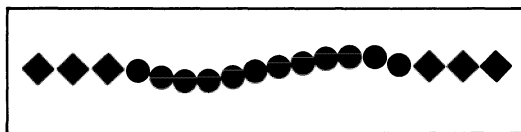


Fig. 1. Simplified representation of a thermoplastic rubber molecule.

(A-B-A-B-A), and so forth.<sup>a</sup> The key requirement is that the thermoplastic rubber molecules terminate with hard, glasslike endblocks which are incompatible with the rubbery midblocks. All such polymers consequently consist of two phases in the solid state—a continuous rubber phase and a basically discontinuous plastic phase which “locks” the rubber molecules in place.

The principles which apply to the simplest version shown in Fig. 1 also apply generally to other configurations. For simplicity, discussions in this chapter will be focused on the sim-

<sup>a</sup>Segmental polyurethanes are not included in this discussion. Their properties and behavior have been discussed elsewhere.<sup>5</sup>

\*deceased



plest version, yet will apply broadly to other structures as well. Discussion will also be focused on two basic classes of thermoplastic rubber. One class consists of block polymers in which the rubbery midblocks of the molecule is an unsaturated rubber. The two types of polymers in this class are the polystyrene-polybutadiene-polystyrene (S-B-S) polymers and the polystyrene-polyisoprene-polystyrene (S-I-S) polymers. The second class of thermoplastic rubber consists of block polymers in which the elastomeric midblock is a saturated olefin rubber. The polymers in this class are the polystyrene-poly(ethylene/butylene)-polystyrene (S-EB-S) polymers and the polystyrene-poly(ethylene/propylene) (S-EP) polymers.

When many A-B-A molecules are combined in the solid phase, a two-phase structure is formed by the clustering of endblocks. An idealized and simplified representation of this is shown in Fig. 2.

The plastic endblocks phase regions, called “domains”, are shown in sphere-like form. Other forms are discussed later. These domains act as crosslinks between the ends of the rubber chains, serving to lock the rubber chains and their inherent entanglements in place. The system acts like a conventionally vulcanized rubber that contains dispersed reactive filler particles.

This physically crosslinked matrix exhibits typical physical properties shown in Table 1. The data represent various neat S-B-S and S-I-S thermoplastic rubber samples cast from toluene solutions.

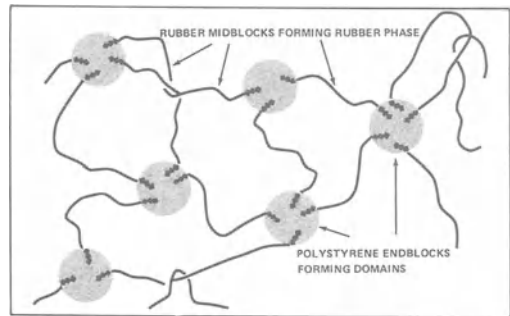


Fig. 2. Idealized two-phase network of thermoplastic rubber molecules.

Table 1. Typical Physical Properties of S-B-S and S-I-S Thermoplastic Rubber at 23°C.

Tensile strength at break ( $T_B$ ), psi	3000–5000
300% Modulus ( $M_{300}$ ), psi	100–400
Elongation at break ( $E_B$ ), %	800–1300
Hardness, Shore A:	30–80

The same range of properties may also be obtained on casting these polymers from a melt. In neither case is chemical vulcanization required. That thermoplastic rubber really is a new class of polymer is depicted in Fig. 3.

Thermoplastic rubber as defined above was first marketed commercially in 1965 by Shell Chemical Company. A list of the trade names, manufacturers, and types of thermoplastic polymers produced is presented in Table 2.

Thermoplastic rubber polymers act as high strength film-formers when used alone or act to increase the cohesive strength or viscosity of systems to which they are added. They dissolve rapidly, without premastication, in a range of low-cost solvents to give useful high solids, low viscosity solutions. They can be mixed readily with many compounding ingredients, and the resulting formulations may be applied to substrates either by solution or by hot-melt techniques. High-tack pressure-sensitive adhesives or nonblocking assembly adhesives may be formulated by varying the types of resins and plasticizers used.

Thermoplastic rubber polymers are resistant to attack by most aqueous reagents, normally have good electrical insulating properties, and

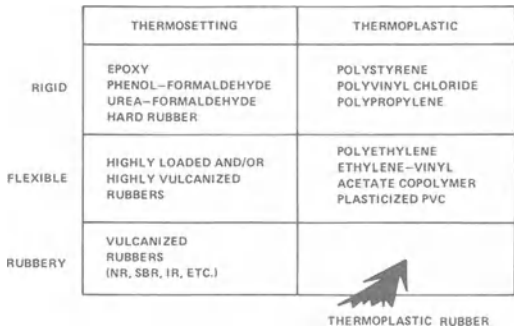


Fig. 3. Polymer classification.

**Table 2. Trade Names of Thermoplastic Rubber.**

Trade Name	Manufacture	Polymer Types
Kraton® D	Shell	S-B-S, S-I-S, (S-B) <sub>n</sub> , (S-I) <sub>n</sub>
Cariflex® TR <sup>a</sup>	Shell	S-B-S, S-I-S
Kraton G	Shell	S-EB-S, S-EP (Diblock)
Europrene® SOL T <sup>a</sup>	Enichem	S-B-S, S-I-S
Stereon®	Firestone	S-B-S
Tufprene® & Asaprene® <sup>a</sup>	Asahi	S-B-S
Finaprene® <sup>a</sup>	Fina	(S-I) <sub>n</sub>
Solprene® <sup>a</sup>	Phillips	(S-B) <sub>n</sub>

<sup>a</sup>Not manufactured in U.S.A.

have excellent low temperature properties. They are soluble in many hydrocarbon solvents and are thermoplastic at elevated temperatures. A measure of solvent resistance and high temperature strength can be imparted by mechanically mixing them with insoluble polymers such as polypropylene or by crosslinking.

The behavior of thermoplastic rubber in adhesives is dependent on (1) the morphology or geometry of the submicroscopic endblock phase as it is dispersed in the rubber matrix, and (2) the compatibility of added ingredients with the two phases present. These topics are discussed in subsequent sections.

### BASIC CONCEPTS—MORPHOLOGY AND COMPATIBILITY

The structure of thermoplastic rubber is unique. It does not behave like conventional elastomers such as natural rubber or styrene-butadiene rubber (SBR) in a number of important respects. The next several sections explain the fundamental principles of its behavior.

#### Thermoplastic Rubber Is A Two-Phase System

Much work has been published on the physical structure of thermoplastic rubber.<sup>6-16</sup> Two glass transition temperature ( $T_g$ ) peaks are found in dynamic mechanical tests with an S-B-S block copolymer.<sup>1</sup> In contrast, only one peak is found in a random SBR copolymer with the same styrene/butadiene ratio. This difference is shown in Fig. 4.

The two peaks in S-B-S polymers indicate that separate polystyrene and polybutadiene phases are present in these block copolymers just as they would be in a physical blend of the

two homopolymers. Only one phase is present in SBR.

In commercial thermoplastic rubbers, the endblock phase is present in the smaller proportion (see Table 2) and is dispersed in a continuous rubber matrix as suggested by Fig. 2. The uniform dispersion of spherical endblock domains shown in this figure, however, is approached only in carefully prepared laboratory samples with low endblock phase concentration. Depending on the endblock phase concentration and on actual processing conditions used to prepare a given sample, the geometry or morphology of the dispersed phase may be sphere-like, rod-like, or plate-like as depicted in Fig. 5.

In the latter two cases, the endblock phase may extend as a continuous plastic network throughout the rubber matrix. This tends to be the case when the endblock phase concentration is above about 20%w. In this situation, as the sample is stretched, the initial stress is borne by the plastic network, and the stress-strain properties are greatly affected as discussed below. The existence of these different morphol-

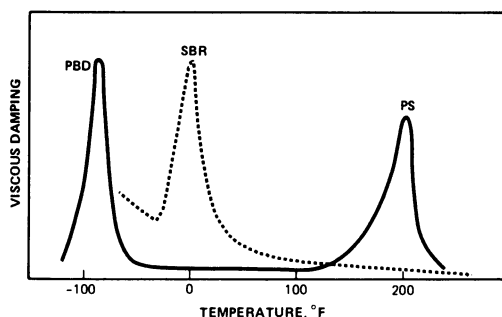


Fig. 4. Glass transition temperatures ( $T_g$ ) in S-B-S and SBR. PBD = Polybutadiene; PS = Polystyrene; SBR = Styrene-butadiene rubber.

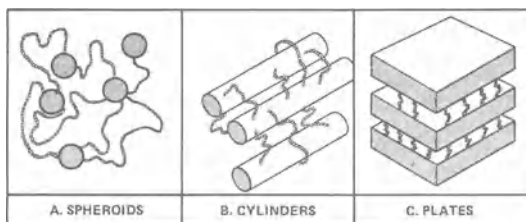


Fig. 5. Polystyrene domain configurations or morphologies.

ogies has been confirmed by electron micrographs.<sup>13</sup>

Under all conditions the dimensions of the dispersed phase are restricted. Since the junctures between the endblocks and midblocks are located at the phase boundary, the domain thickness is limited to the distance which can be reached by the endblock segments extending into the domains from opposite sides. For commercial polymers, domain thicknesses have been both calculated and measured to be a few hundred Angstrom units or only a small fraction of the wavelength of visible light. If the domains are spheroidal, they do not scatter light. Thus, pure thermoplastic rubber is generally transparent, in spite of the large differences in refractive index between the two phases. With rod-like or plate-like morphologies some light scattering and turbidity may exist.

#### Additives Are Compatible With One Phase, Both Phases, or Neither Phase

Information on how additives, such as resins, plasticizers, and other polymers, distribute between the two phases in thermoplastic rubbers is important in interpreting the behavior of adhesive formulations. For example, adding a resin which dissolves solely in the plastic endblock phase may produce a hard, nontacky material, while adding a resin which dissolves only in the rubber phase may result in an extremely sticky, soft, flexible composition. Yet both mixtures may have high cohesive strength as long as the endblock domains form properly.

The solubility parameter ( $\delta$ ) and molecular weight of an additive determine how it will distribute between the two phases present in thermoplastic rubber. Solubility parameter

(discussed more fully in the appendix at the end of this chapter) is a basic property characteristic of every solid or liquid including polymers, resins, plasticizers, solvents, stabilizers, and fillers. Expressed in units of  $(\text{cal}/\text{cm}^3)^{1/2}$  called "hildebrands," the solubility parameters of interest in this chapter fall generally in the range 6 to 12 hildebrands. If two substances have solubility parameters close enough together, they will tend to be mutually soluble. The higher the molecular weight of the two materials, the smaller the difference between their solubility parameters must be for mutual solubility to occur. For example, isooctane ( $\delta = 6.85$ ) and toluene ( $\delta = 8.9$ ), both low molecular weight solvents, are mutually soluble. On the other hand, the high molecular weight polymers, polyisoprene ( $\delta = 8.1$ ) and polybutadiene ( $\delta = 8.4$ ), will not mix on a molecular scale. Similarly, the polystyrene endblock phase ( $\delta = 9.1$ ) and the rubber matrix ( $\delta = 8.1$  or  $8.4$ ) in commercial thermoplastic rubbers do not mix and therefore form the two-phase systems shown in Figs. 2 and 5.

Solubility parameter and molecular weight data are not readily available for many adhesive components. However, compatibility data are available for a number of resins, plasticizers, and solvents. Some of them are listed in later sections or in the literature.<sup>19,22-27</sup> In any particular case, information on specific components can be obtained by simple tests. For example, the solubility range of a given formulation can be determined by attempting to dissolve the components in a series of solvents of interest. One can also determine qualitatively with which phase of a thermoplastic rubber a given resin is compatible as follows: Cast a thin film from a toluene solution of (1) a 1 to 1 mixture of the resin and crystal grade polystyrene and (2) a 1 to 1 mixture of the resin and natural rubber or polyisoprene for S-I-S polymers or the resin and polybutadiene for S-B-S polymers. Clarity of the dried film indicates mutual solubility; turbidity indicates phase separation. Qualitative interpretation of experimental observations on a new system in terms of the above compatibility concepts can often suggest means of changing the system to improve its performance in the desired direction.

## PHYSICAL PROPERTIES OF THERMOPLASTIC RUBBER—ALONE AND IN SIMPLE MIXTURES

This section discusses specific examples of the concepts introduced in the previous section. The general principles illustrated here are important to the effective use and modification of the starting formulations presented later.

### Stress-Strain Properties

The cohesive strength of an adhesive film is closely related to its stress-strain behavior. The stress-strain properties of thermoplastic rubber formulations are in turn closely related to the volume ratio of endblock phase to midblock phase and to the morphology of these two phases.

**Effect of Phase Ratio.** As the endblock concentration in an unfilled thermoplastic rubber increases, the shape of the stress-strain curves change as shown in Fig. 6. These particular curves apply to solution-cast films prepared from a series of experimental S-B-S polymers. The total molecular weight for each polymer was held constant; only the styrene content was varied.

At concentrations of 20–30%w, the stress-strain curve resembles that of a vulcanized rub-

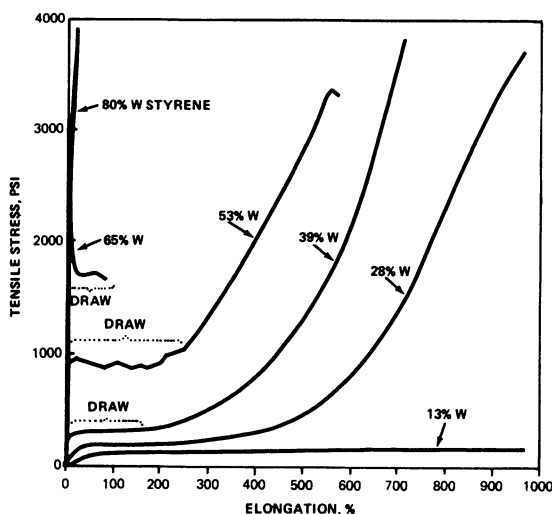


Fig. 6. Effect of endblock concentration on S-B-S tensile properties.

ber. At concentrations above about 33%w, the phenomenon of “drawing” commonly exhibited by thermoplastics appears. This occurs when a continuous rod-like or plate-like endblock network exists as suggested in Fig. 5. When such a sample is stretched, an initial yield stress is observed. Then, as the relatively weak plastic structure is disrupted by further elongation, drawing occurs. When the stress is released, the plastic network will gradually reform. Higher temperatures will speed reforming of the plastic network. At high endblock concentrations, the plastic phase is continuous and the midblock phase dispersed to give a system resembling high impact polystyrene.

**Effects of Additives.** The ratio of endblock phase to midblock phase can be varied by adding materials which associate preferentially with one phase or the other. Coumarone-indene resins, for example, associate with the endblock phase in S-B-S and S-I-S polymers. Figure 7 shows how the initial portion of the stress-strain curve of the neat polymer, Curve B, is shifted upward to Curve A when the endblock phase concentration is increased by adding a resin of that type. Curve C shows how the reverse occurs when, for example, a tackifying resin or a plasticizing oil which associates with the rubber phase is present instead.

**Effect of Previous Processing.** By proper selection of processing conditions, both drawing and nondrawing samples can be prepared from the same thermoplastic rubber formula-

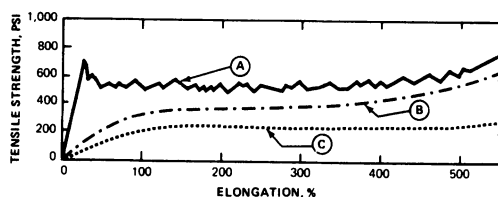


Fig. 7. Effect of endblock and midblock resins or preferential solvents on endblock morphology and tensile properties.

Curve	Resin Type	Casting Solvent
A	Endblock	Methyl ethyl ketone (MEK)
B	None	Toluene
C	Midblock	C <sub>6</sub> -C <sub>7</sub> Paraffin hydrocarbons

tion when the endblock concentration is above about 20%w. Thus, endblock morphology can be modified in a third way. If a film is cast from a solvent which is, or which becomes during evaporation, good for the endblock phase and poor for the rubber phase, the formation of a continuous endblock phase is favored. Drawing may then occur as indicated by Curve A of Fig. 7 discussed in the previous paragraph. When the opposite type of solvent is used, the drawing is inhibited and a rubbery film is produced with characteristics of Curve C in Fig. 7.

Similar effects can be obtained with hot-melt formulations. Subjecting such a mixture to high shear and quickly quenching it to room temperature, produces behavior indicated by Curve A in Fig. 7. Alternatively, using no shear and slowly cooling to room temperature produces behavior indicated by Curve C in Fig. 7.

These effects of solvent and thermal-shear history are not equilibrium states. Annealing samples of this sort at 140°F, for example, will tend to bring the curves in Fig. 7 closer to Curve B. Nevertheless, such techniques applied alone or in conjunction with others may be very useful in tailoring a product to a specific application.

### Glass Transition Temperatures and Service Temperature Range

The temperature range over which thermoplastic rubber compositions can be used as elastomeric solids depends on the glass transition temperatures ( $T_g$ ) for the two polymer phases. As illustrated in Fig. 4, this useful range lies between the  $T_g$  of the rubber phase and the  $T_g$  of the endblock phase. Below the  $T_g$  of the rubber phase, the midblocks become hard and brittle. Above the  $T_g$  of the plastic phase, the domains soften and cease to crosslink the rubber midblocks.

Each  $T_g$  depends on the nature of that polymer segment itself and also on the nature of any materials dissolved in it. Figure 8 illustrates how the normal  $T_g$  of about 210°F for the endblock phase in an S-B-S polymer can be shifted by adding endblock compatible resins of differing softening points.

The limit of upper service temperature at a

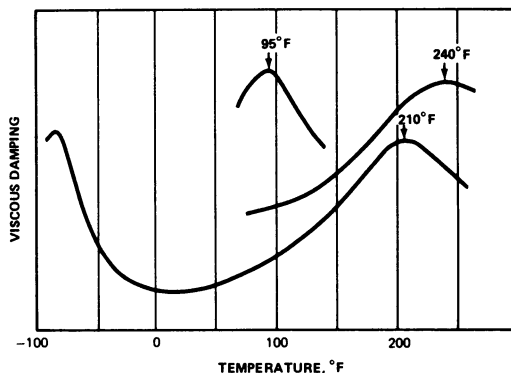


Fig. 8. Effect of endblock resins on endblock glass transition temperature ( $T_g$ ).

$T_g = 210^\circ\text{F}$ : No resin.

$T_g = 240^\circ\text{F}$ : 75 phr LX-685, 180 (softening point 150°C).

$T_g = 95^\circ\text{F}$ : 75 phr Piccovar AP-25 (softening point 25°C).

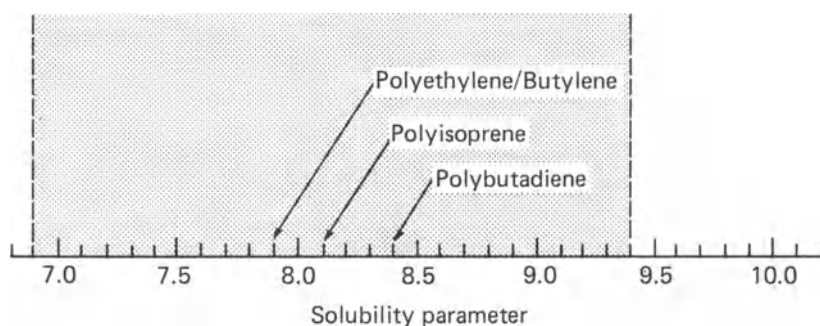
given stress may be shifted upward by adding an endblock compatible resin with a high softening point. Conversely, a similar low softening point resin can lower the temperature at which a mixture softens and becomes heat bondable. The addition of resins and plasticizers which are soluble in the midblock phase similarly change the low temperature  $T_g$  of the rubber phase.

### Solubility and Solution Viscosity

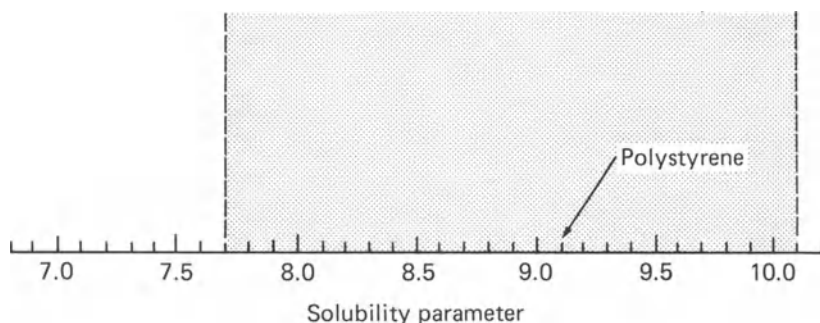
The behavior of thermoplastic rubber toward solvents is unique because of the two segments present in each molecule. Each segment retains its own solubility properties.

**Solvent Selection.** As mentioned above, a given polymer will dissolve only in solvents whose solubility parameters are close to that of the polymer. In thermoplastic rubber, two solubility parameters are involved, one for the endblock and one for the midblock. A "good" solvent for a thermoplastic rubber must therefore be one which dissolves both endblocks and midblocks.

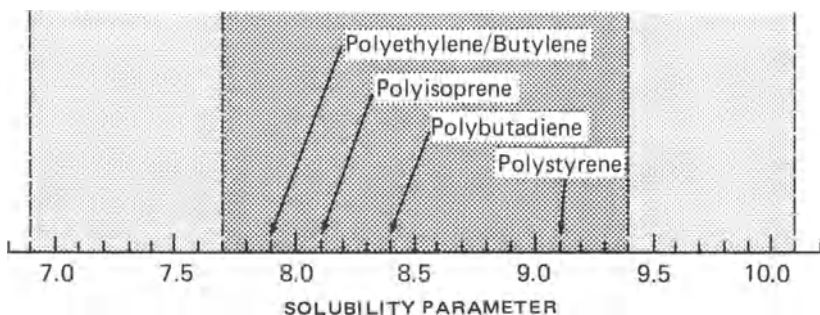
To illustrate, Fig. 9-A indicates the approximate range of solvents for polydiene midblocks. The boundaries are not sharp near the extremes because the polymer molecules tend to collapse while still solvated. The location of



(a) Solubility parameter range of solvents useful for rubber phase.



(b) Solubility parameter range of solvents useful for polystyrene phase.



(c) Solubility parameter range of solvents useful for KRATON rubber.

Fig. 9. Solvents for thermoplastic rubber.

the boundaries and several solvents are shown for illustrative purposes.

Figure 9-B indicates in a similar way, the range of solvents for polystyrene endblocks.

Figure 9C shows what happens when both types of polymer are combined in a single block copolymer molecule. A central range of solvents readily dissolves both blocks and gives low viscosity solutions. With solvents at the lower solubility parameter end, the polystyrene

endblocks tend to remain associated and form what might be termed solvated endblock domains. In this region, solution viscosity increases rapidly with decreasing solubility parameter until rigid crosslinked gels are formed. With solvents at the high solubility parameter end, the situation is somewhat different. First, the midblocks become less and less soluble and tend to associate together while the endblocks are highly solvated. Opalescent so-

lutions with time-dependent viscosities are formed. Thermoplastic rubber crumb can be dispersed in this sort of borderline solvent (for example, methyl ethyl ketone).

A practical application of these principles is shown in Fig. 10. The curves represent the viscosities of 15%w solutions of an S-B-S thermoplastic rubber in a series of *n*-hexane/toluene blends. As the toluene concentration is reduced, the viscosity increases rapidly due to endblock association as the endblock domains tend to precipitate from solution. About 20%w toluene must be present in the mixed solvent if low viscosities are to be achieved in this situation. The solvent mixtures can also be characterized by solubility parameter and Kauri Butanol Value as shown on the abscissa. A solubility parameter of 7.6 or above and a Kauri Butanol Value of 37 or higher are required for low solution viscosity in this case.

In the selection of a solvent, one should consider all soluble low molecular weight compo-

nents present in the thermoplastic rubber formulation. Resins and plasticizers are usually the most important components in this respect. As an example, the effect of adding 100 phr of a tackifying resin (Foral 85) to a 15%w solution of an S-B-S polymer is shown in Fig. 11. The presence of the resin has made the toluene/*n*-hexane blends better endblock solvents, so that less toluene percentage is required to obtain minimum viscosity even at the higher total solids concentration.

### Viscosity and Polymer Concentration.

Thermoplastic rubbers without premastication have lower solution viscosities than do conventional elastomers such as SBR, natural rubber, and neoprene after milling. This is because thermoplastic rubbers have low, precisely-controlled molecular weights. Figure 12 compares the viscosities of a typical S-B-S polymer with two conventional elastomers in toluene solution.

### Melt Viscosity

The viscosities of thermoplastic rubber melts are strongly non-Newtonian, decreasing as

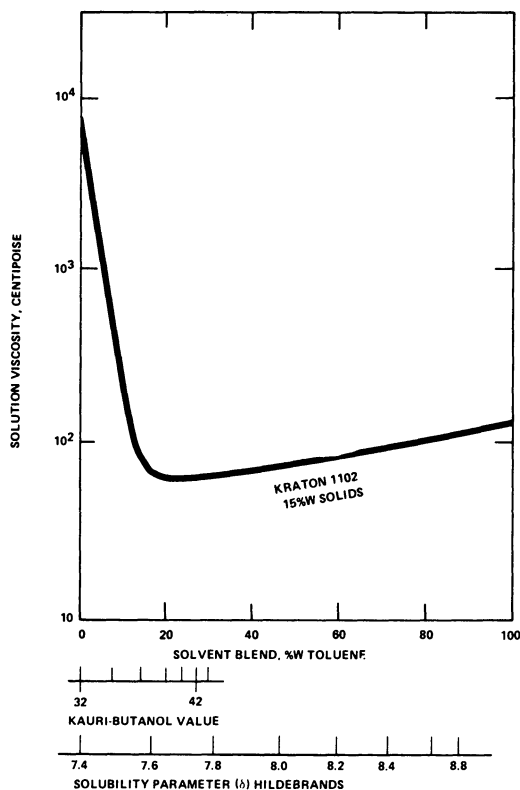


Fig. 10. Viscosity of S-B-S thermoplastic rubber in poor endblock solvents.

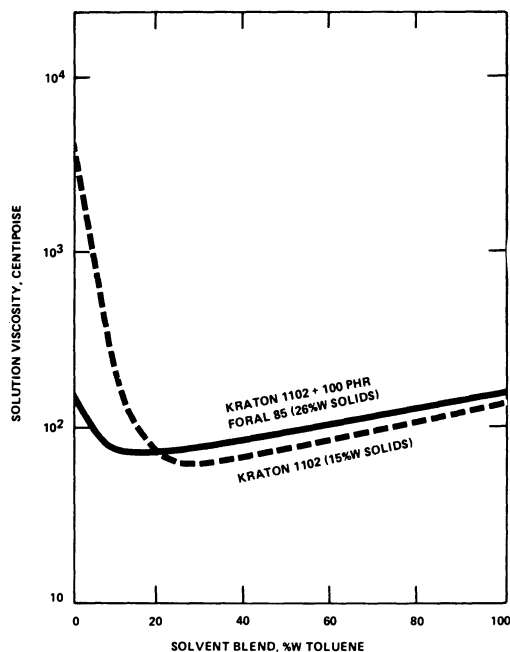


Fig. 11. Effect of a resin on the viscosity of S-B-S thermoplastic rubber in poor endblock solvents.

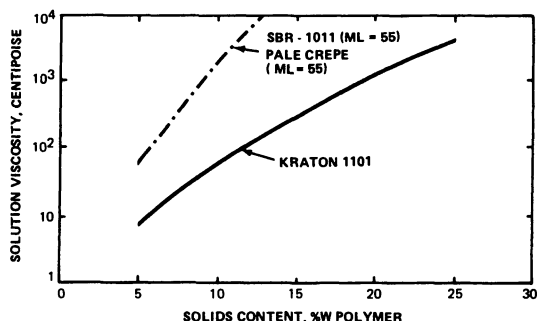


Fig. 12. Solution viscosity of polymers in toluene.

shear rate increases. Figure 13 shows the melt viscosity of an S-B-S thermoplastic rubber at 350°F. Also shown is the plasticizing effect of 100 phr of a tackifying resin. Through selection of appropriate types and amounts of resins and plasticizers, the melt viscosity of a given hot-melt adhesive can be controlled over a wide range.

The effect of temperature on melt viscosity is illustrated in Fig. 14. Here the viscosity of a typical S-B-S polymer is shown at three shear rates. It is important to note the long plateau followed by a rapid increase in viscosity on cooling. Through control of application temperature, either long or short open times followed by rapid setup can be achieved. These characteristics are advantageous in high speed packaging where rapid hot tack buildup is de-

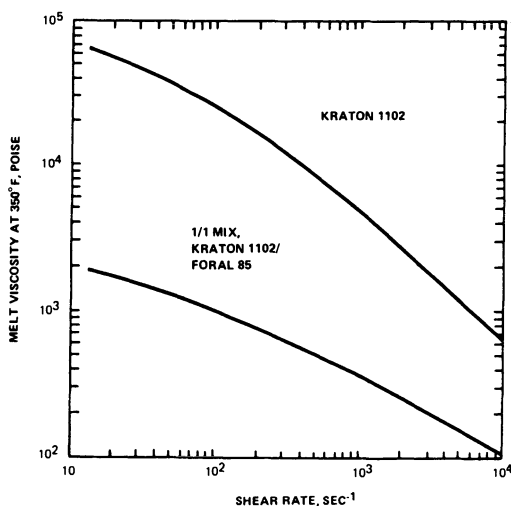


Fig. 13. Melt viscosities of S-B-S and S-B-S/resin blends.

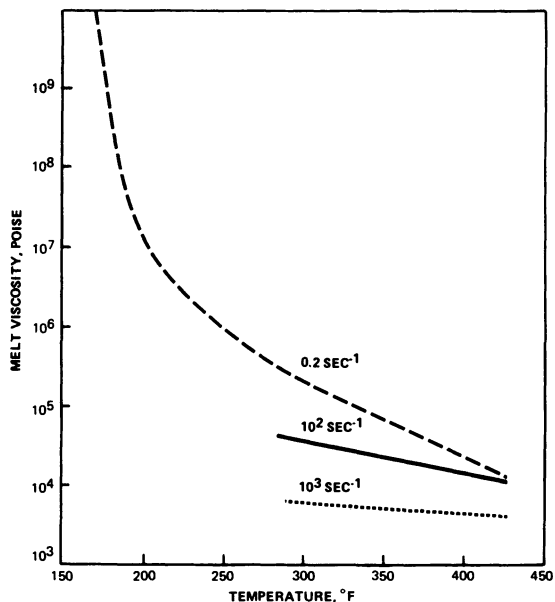


Fig. 14. Effect of temperature on S-B-S melt viscosity.

sired and in product assembly applications where long open time is desired.

### Permeability to Nitrogen and Water Vapor

The vapor permeability of thermoplastic rubbers with polydiene midblocks is similar to that of the rubber which forms the midblock. However, as the fraction of endblock is increased, as for example by adding endblock compatible resins, the permeability is somewhat reduced. Conversely, as the rubber phase fraction is increased, for example by adding a midblock compatible oil, the nitrogen permeability increases. While the permeability of thermoplastic rubbers is about the same as SBR, natural rubber, and polybutadiene, it is much higher than polyolefins and other materials used in packaging. This can be an advantage where high air or moisture vapor transmission is desired.

### FORMULATING INGREDIENTS

In this section, major types of formulating ingredients and their roles in the design of adhesives are discussed. This generalized information is focused in the section on the formulation of specific adhesives. The formulator



will find a recent tabulation of adhesive raw materials and suppliers useful in selecting specific components.<sup>17</sup>

### Which Resins?

Resins for use with thermoplastic rubbers are selected to perform one or more functions. To aid in the selection process, resins can be grouped first according to their tendency to associate with one phase or the other in thermoplastic rubber. Within these groups, other subdivisions can be made depending on the effect on adhesive properties.

#### Predominantly Endblock Compatible Resins.

Polyaromatics, cumarone-indene resins, and other high solubility parameter resins derived from coal tar or petroleum and having softening points above about 85°C tend to associate with the polystyrene endblocks and not with the polydiene midblocks. As the molecular weights or softening points of these resins are lowered, their solubility in the midblocks increases. A list of typical commercial resins in this category is presented in Table 3.

Resins in this category are used to improve the specific adhesion of the endblock phase, to adjust melt viscosity, and to control the modulus of the resulting adhesive formulation. Addition of predominantly endblock associating resins tends to stiffen the formulation and increase the tendency to draw as discussed previously. This occurs as the fraction of endblock

phase increases and its morphology becomes more rod-like or plate-like.

High softening point resins in this category may also tend to increase the glass transition temperatures ( $T_g$ ) of the endblock phase (Fig. 8). This results in the formulation retaining its cohesive strength at higher temperatures. Resins effective in this direction are indicated in Table 3 by their effect on the Shear Adhesion Failure Temperature<sup>a</sup> of an adhesive formulation.

Low softening point resins have the reverse effect, namely to lower the tensile strength at elevated temperatures, to cause the tack in heat activated adhesives to develop at lower temperatures, and to reduce the temperature at which the formulation can be handled as a hot-melt.

#### Predominantly Midblock Compatible Resins.

Aliphatic olefin derived resins, rosin esters, polyterpenes, and terpene phenolic resins derived from petroleum or terpentine sources and having relatively low solubility parameters tend to associate with the polydiene midblocks and not with the polystyrene endblocks. As the molecular weights or softening points of these resins are lowered, their solubility in the end-

<sup>a</sup>Shear Adhesion Failure Temperature (SAFT): Temperature at which complete failure of a 1 in. × 1 in. shear adhesion sample (polyester to polyester) occurs under a load of 1 kg in a circulating air chamber whose temperature is raised 40°F per hour starting at 100°F.

**Table 3. Endblock-Phase-Associating Resins for Thermoplastic Rubbers.**

<i>Trade Name</i>	<i>Softening Point, °C</i>	<i>Chemical Type</i>	<i>Supplier</i>
Amoco® 18 Series	100, 115, 145	Alphamethyl styrene	Amoco
Kristalex® Series	85–140	Alphamethyl styrene	Hercules
Piccotex® Series	75–120	Alphamethyl styrene/vinyl toluene	Hercules
Nevchem® Series	100–140	Aromatic hydrocarbons	Neville
Picco 6000 Series	70–140	Aromatic hydrocarbons	Hercules
Nevindene® LX Series	100–150	Heat reactive hydrocarbon	Neville
Cumar® Series	10–130	Coumarone-indene	Neville
Cumar LX-509	155	Coumarone-indene	Neville
Piccovar® AP Series	Liquid <sup>a</sup>	Alkylaryl resin	Hercules
Piccovar 130	130	Alkyl aromatic polyindene	Hercules

<sup>a</sup>Because of the low molecular weight, these resins are soluble in both endblock and midblock phases of thermoplastic rubbers.

blocks increase. A partial list of commercial resins in this category is presented in Table 4.

Resins in this category are used to impart pressure-sensitive tack, to improve the specific adhesion of the midblock phase toward polar substrates, as processing aids for the midblock phase, and to control the modulus of the resulting adhesive formulations. Addition of predominantly midblock associating resins tends to soften the formulation and reduce the tendency to draw as discussed earlier. These latter effects occur as the addition of midblock resin increases the fraction of midblock phase in the system and causes the morphology of the dispersed endblock phase to become more sphere-like (less continuous).

Resins in this category may also increase the glass transition temperature ( $T_g$ ) of the mid-

block phase. This can result in reduction of low temperature flexibility. Partial compensation for this reduction can be obtained through the use of midblock plasticizers. There may also be some effect on the upper service temperature as the result of some unavoidable plasticizing of the endblocks.

### Why Plasticizers?

Plasticizers may perform the following useful functions in adhesives based on thermoplastic rubbers: decrease hardness and modulus, eliminate drawing, enhance pressure-sensitive tack, improve low temperature flexibility, reduce melt and solution viscosity, decrease cohesive strength or increase plasticity if desired, and substantially lower raw material costs. The

**Table 4. Rubber-Phase-Associating Resins for Thermoplastic Rubbers.**

<i>Trade Name</i>	<i>Softening Point, °C</i>	<i>Chemical Type</i>	<i>Supplier</i>
Adtac® B Series	10, 25	Synthetic C <sub>5</sub>	Hercules
Betaprene® BC	100, 115	Synthetic C <sub>5</sub>	Reichhold
Eastman® Resin	100, 115, 130	Synthetic C <sub>5</sub>	Eastman
Escorez® 1300 Series	80, 100, 120	Synthetic C <sub>5</sub>	Exxon
Hercotac® 95	100	Synthetic C <sub>5</sub>	Hercules
Nevtac® Series	80, 100, 115, 130	Synthetic C <sub>5</sub>	Neville
Piccopale® HM-200	100	Synthetic C <sub>5</sub>	Hercules
Piccotac®	93, 100	Synthetic C <sub>5</sub>	Hercules
Quinton® Series	85, 100	Synthetic C <sub>5</sub>	Nippon Zeon
Sta-Tac® R	100	Synthetic C <sub>5</sub>	Reichhold
Super Nevtac® 99	99	Synthetic C <sub>5</sub>	Neville
Super Sta-Tac	80, 100	Synthetic C <sub>5</sub>	Reichhold
Wingtac® Series	10, 75, 85, 95, 115	Synthetic C <sub>5</sub>	Goodyear
Arkon® P Series	70, 85, 115, 125	Hydrogenated Hydrocarbon	Arakawa
Escorez 5000 Series	85, 105, 125	Hydrogenated Hydrocarbon	Exxon
Regalrez® Series	18, 76, 94, 126	Hydrogenated Hydrocarbon	Hercules
Super Nirez® Series	100, 120	Hydrogenated Hydrocarbon	Reichhold
Nirez® Series		Polyterpene	Reichhold
Piccofyn® A100	100	Terpene phenolic	Hercules
Piccolyte® A	85, 115, 135	Polyterpene	Hercules
Piccolyte S10	10	Polyterpene	Hercules
Zonarez® 7000 Series	85, 100, 115, 125	Polyterpene	Arizona
Zonarez B Series	10, 100, 125	Polyterpene	Arizona
Zonatac® Series	85, 100, 115	Polyterpene	Arizona
Foral® Series	82, 104	Rosin Ester	Hercules
Hercolyn® D	Liquid	Rosin Ester	Hercules
Pentalyn® H	104	Rosin Ester	Hercules
Staybelite Ester 10	Liquid	Rosin Ester	Hercules
Sylvatac® Series	70-110	Rosin Ester	Sylvachem
Zonester® Series	83, 95	Rosin Ester	Arizona
Piccovar® AP Series	Liquid <sup>a</sup>	Alkylaryl	Hercules

<sup>a</sup>Because of the low molecular weight, these resins are soluble in both endblock and midblock phases of thermoplastic rubbers.

properties of a plasticized formulation are highly dependent upon the plasticizer composition, its solubility parameter, and its molecular weight.

**Selecting a Plasticizer for High Performance Adhesives.** The ideal plasticizer for use with thermoplastic rubbers in high performance adhesives is one which is completely insoluble in the endblock phase, completely miscible with the midblock phase, and low in cost. Low volatility, low viscosity, low density, and resistance to degradation are also desirable characteristics. Various hydrocarbon oils whose average solubility parameters are below those of the midblocks, but not too far below, satisfy these requirements reasonably well.

Process oils are usually mixtures of molecular species which can be classed as aromatic, naphthenic, and paraffinic. When these oils are added to thermoplastic rubber, fractionation may occur with the aromatics concentrating in the endblock domains. Reduced cohesive strength at ambient and elevated temperatures

typically results from using oils containing as little as 2–3% aromatics.

Typical hydrocarbon plasticizing oils and oligomers are listed in Table 5. They are arranged in order of increasing solubility parameter. Oils with the lowest solubility parameter and highest molecular weight are the least soluble in the endblock phase and will have least effect on high temperature strength of thermoplastic rubber formulations. These same oils will also have the lowest solubility in the rubber phase and thus the most tendency to bleed-out at high concentrations.

Swelling data for S–B–S in each oil are also listed in Table 5. Although actual bleed-out tests are required to establish acceptable oil levels for each application, there is usually no tendency for oil to bleed out of compositions containing less than half the amount absorbed during the swelling test. The presence of rubber-compatible resins reduces the tendency further. Selection of a plasticizer involves balancing the various plasticizer characteristics to best fit any specific application.

The effect of oil type on the tensile properties of a compression molded S–I–S polymer is

**Table 5. Properties of Plasticizing Oils.**

Trade Name	Supplier	Solubility Parameter $\delta$ , <sup>a</sup> Hildebrands	Average Mole Weight <sup>b</sup>	Specific Gravity (15.6°C)	Volatility Loss, <sup>c</sup> Weight %	Oil Absorbed, <sup>d</sup> phr
Polypropene D-60	Amoco	6.55	800	0.86	0.1	25
Polybutene-18	Chevron	6.95	600	0.88	0.1	39
Tufflo 6206	Arco	7.06	660	0.88	0.05	31
Polybutene-12	Chevron	(7.04)	530	0.88	—	(53)
Tufflo 6056	Arco	7.18	550	0.87	0.3	56
Polybutene-8	Chevron	(7.18)	440	0.86	—	(75)
Kaydol	Witco	7.34	480	0.89	—	82
Tufflo 6026	Arco	7.29	410	0.86	1.0	76
Polybutene-6	Chevron	7.34	315	0.84	10.0	103
Tufflo 6016	Arco	7.51	390	0.85	2.0	106
Tufflo 6204	Arco	7.60	440	0.92	0.5	96
Shellflex® 371	Shell	7.60	410	0.90	0.9	112
Tufflo 6094	Arco	7.60	410	0.92	0.8	95
Tufflo 6054	Arco	(7.66)	380	0.92	1.3	(127)
Tufflo 6014	Arco	7.73	320	0.89	12.0	214

<sup>a</sup>Calculated from experimentally determined surface tension, average mole weight, and specific gravity. Values in parentheses were interpolated.

<sup>b</sup>By ebullioscopic methods of Mechrolah osmometer.

<sup>c</sup>22 hours and 107°C.

<sup>d</sup>Grams of oil absorbed by 500–1000 micron films of Kraton® D1101 Rubber at room temperature per 100 grams original weight after soaking 100 hr. Films were prepared by casting from toluene solution on mercury and drying very slowly. Values in parentheses were interpolated or extrapolated from related data.

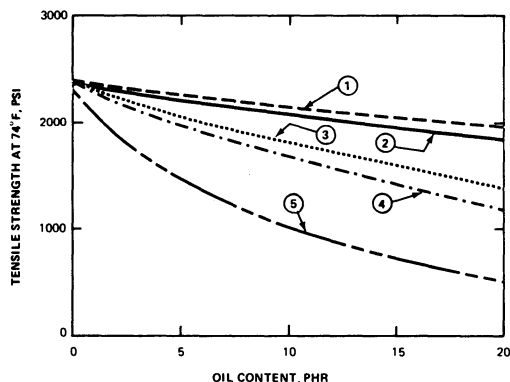


Fig. 15. Effect of oil type (see Table 5) on the tensile strength of an S-I-S thermoplastic rubber.

1. Decrease due to dilution alone (calculated).
2. Tufflo 6206 oil (observed).
3. Tufflo 6204 oil (observed).
4. Shellflex® 371 (observed).
5. Shellflex 314 (observed).

shown in Fig. 15. These curves lie in the order of increasing solubility parameter and aromatic content shown in Table 5.

**Plasticizers Which Reduce Cohesive Strength.** Plasticizers which are readily compatible with the polystyrene endblocks prevent the formation of strong crosslinks between the rubber molecules. Endblock domains will form as a separate phase, but instead of being hard and rigid at room temperature, they will be soft and fluid. Stress applied to the network will cause irreversible flow.

An example of a plasticizer which destroys cohesive strength is dioctylphthalate (DOP), commonly used in plasticized polyvinyl chloride (PVC) compositions. A relatively small amount of DOP added to an S-B-S thermoplastic rubber reduces the ultimate tensile strength from above 4000 psi to zero. Low molecular weight liquid tackifying resins are also often soluble in both phases and tend to reduce cohesive strength. However, they may still be useful in some adhesive applications.

Adhesives based on a thermoplastic rubber with polystyrene endblocks should be carefully tested when intended for direct contact with PVC highly plasticized with DOP. The latter can diffuse into the rubber phase and destroy the cohesive strength as discussed above. The most effective way to prevent the loss of co-

hesive strength in a situation of this type is to replace the DOP with a nonmigrating plasticizer.<sup>a</sup> Another way is to use a primer or barrier coating which restricts the tendency for plasticizer migration.

### Other High Polymers

**Elastomers.** Low levels of thermoplastic rubber added to adhesives based on conventional unvulcanized rubber like natural rubber, polyisoprene, and SBR, upgrade cohesive strength, lower solution viscosity, and may improve adhesive strength. At the other end of the scale, use of a limited amount of a conventional rubber in a thermoplastic rubber formulation may increase solution or melt viscosity and lower costs with limited loss in cohesive strength or other properties.

The degree of compatibility between high polymers must be considered in formulating adhesives. S-I-S polymers are essentially miscible with polyisoprene and natural rubber. S-B-S polymers mix well with SBR and polybutadiene. In other combinations, however, turbidity of cast films, slow phase separation in solution, and other evidence of molecular incompatibility may appear. Nevertheless, rubbers of the incompatible type, including neoprene and nitrile rubbers, may form commercially useful mixtures if mixing problems, tendency to phase separate, and turbidity, etc. are appropriately handled. Methods of offsetting incompatibility include use of high shear mixing, formulating for high solution viscosities, mixing immediately before use, and inclusion of compatibilizing resins in the formulation.

Blending thermoplastic rubber into ethylenevinyl acetate (EVA) polymers with low to medium vinyl acetate content is roughly equivalent to increasing the vinyl acetate content. The mixtures become softer and exhibit better flexibility at ambient and low temperatures.

**Thermoplastics.** Specific desirable characteristics may be obtained by blending a wide

<sup>a</sup>For example, Paraplex G-50 or G-54, intermediate and medium high molecular weight polyesters (Rohm and Haas Company).

range of plastic materials into thermoplastic rubber. A third phase is formed by three materials. They can be made into continuous networks by mechanical mixing and applying under high shear conditions. Polystyrene (crystal grade homopolymer), for example, can be blended in solution or melt mixed to increase hardness and modify other physical properties. Crystalline polyethylene and crystalline polypropylene can also be blended in a high shear mixer to raise service temperature limits or to increase solvent resistance. Polar polymers may increase adhesion to metal and polar surfaces.

### What About Fillers?

Nonreinforcing fillers—clay, talcs, whittings, etc.—may be used to increase hardness, modulus, abrasion resistance, density, and to lower raw material costs. Carbon black, which can be used as a pigment and screening ultraviolet stabilizer, forms permanent gel structures with the unsaturated midblocks. This reduces solubility and thermoplasticity. Thermoplastic rubbers generally will tolerate high filler levels while retaining satisfactory cohesive strength.

### Blends with Asphalt

Asphalt is a low cost thermoplastic material which is highly temperature dependent. The addition of a thermoplastic rubber at 1–5%w in an appropriately selected asphalt greatly reduces the dependence of viscosity on temperature. Useful operating temperature ranges can often be doubled in this manner.

The addition of a thermoplastic rubber at 10–30%w produces a truly thermoplastic product with elasticity, resilience, and high adhesive strength. Such mixtures can form the basis for a variety of sealants as discussed in the section on permanent crosslinking. Although the selection of the asphalt and its modifications with aromatic or paraffinic oils is not simple, a balance between resistance to phase separation at 300°F and the formation of a coherent network at ambient temperatures can be obtained by empirical tests.

### Blends With Paraffin Waxes

Paraffin waxes represent potentially useful low cost diluents or, conversely, thermoplastic rub-

bers represent potentially useful flexibilizers and tougheners for wax. However, when thermoplastic rubber and wax are mixed in solution or at elevated temperature, they tend to separate on cooling as the wax crystallizes. Low levels of wax can therefore function as anti-blocking agents. Physically stable three-component mixtures which include an appropriate resin (e.g., a polyterpene) can be prepared. Microcrystalline waxes tend to form more physically stable mixtures than do paraffinic types, but are less chemically stable at mixing and application temperatures.

## MIXING AND APPLICATION

Adhesive formulations are most frequently prepared from thermoplastic rubber by solution or hot-melt techniques because commercial thermoplastic rubber is available in dry form only, usually as crumb or pellets. However, formulations can be prepared as emulsions or as powders if desired.

### Solution Compounding and Application

Solvating the plastic endblock domains serves to “unlock” the physically crosslinked rubber network. Consequently, solution blending of thermoplastic rubber with resins, plasticizers, fillers, etc., requires a solvent which will dissolve the endblocks as well as the rubber midblocks. The selection of solvents was discussed previously.

### Dissolving Thermoplastic Rubber Crumb.

The dissolving process may be carried out in various types of equipment which provide adequate shearing action to the solvent/crumb mixture. Suitable equipment includes: churns or stirred vessels, planetary (Hobart-type) mixers, and internal (Sigma blade type) mixers. Enough shear must be used to prevent agglomeration of the swollen crumb into large lumps.

Short dissolving times are assisted by use of high shear, small rubber particle size, and high temperatures. The use of solvents which are poor for either the rubber phase or endblock phase will increase the dissolving time. Low molecular weight and small particle size generally make dissolving times for thermoplastic

rubber much shorter than those for masticated natural rubber or SBR in good solvent systems.

#### **Static Electricity Safety Precautions.**

Because of the small particle size and insulating nature of thermoplastic rubber, pouring rubber crumb from shipping containers directly into a processing vessel can generate sufficient static electric charge to produce sparks capable of igniting combustible vapor mixtures. The chance for ignition must be guarded against through such measures as proper polymer handling methods, equipment design, bleeding off the charge, or blanketing with inert gas. Agglomerated crumb should not be separated in an explosive atmosphere. Conveyor systems should minimize abrading, scuffing, or rubbing of the crumb. Equipment should be properly grounded. Surface conductivity of the crumb may be improved to favor dissipation of surface charge by passing the crumb through humid air, dusting it with antistatic agents, or dusting it with conductive inorganic fillers. Radioactive static electricity discharge devices may also be used.

#### **Application of Solutions to Substrates.**

Formulated thermoplastic rubber solutions can be applied to various substrates with conventional equipment such as doctor blades, roll coaters, etc. Solution viscosity can be adjusted both through solids concentration and solvent composition as discussed earlier.

A significant advantage of thermoplastic rubber solutions is their faster drying rate in film form compared to solutions of conventional elastomers. When 1 mil films (dry basis) were cast from 10%w toluene solutions, a typical S-I-S polymer reached a given level of residual solvent in 90% of the time required for natural rubber. The films were dried in an 86°F recirculating air oven. If the comparisons were made between solutions of the same solution viscosity (a more practical case), the drying times for the thermoplastic rubbers would be roughly half those for SBR or natural rubber.

#### **Melt Mixing and Processing**

Heating the endblock domains above the glass transition temperature ( $T_g$ ) of the endblocks,

about 210°F for polystyrene, “unlocks” the physically crosslinked rubber network. Application of shear stress then makes possible mixing with other materials and application of the melt to substrates. As discussed earlier, the melt viscosity decreases as the shear stress or shear rate increases. Mixing efficiency is then improved.

With commercial S-B-S and S-I-S thermoplastic rubbers, 250 to 400°F is the normal range for mixing and application. Temperatures above 350°F may lead to excessive oxidative degradation of the rubber network and above 425°F to thermal degradation. At temperatures below 250°F, the viscosity becomes so high that mechanical breakdown of the rubber may occur. Since oxidative degradation is reduced by lowering temperature, the preferred mixing method is in high shear equipment at 275–325°F.

**Batch Mixing Equipment.** Melt mixing can be carried out in a variety of heated mixing equipment. In order of increasing effectiveness, these include: vessels stirred with propellers, vessels with high shear (Cowles-type) dispersers, planetary mixers (Hobart-type), internal mixers (Sigma-blade or Banbury type), and modifications of these.

In low shear mixers, resins, plasticizers, and stabilizers should be melted first and thermoplastic rubber crumb added incrementally. Fillers should be added last. In high shear devices, the order of time of adding the various components is also important to minimize mixing cycle time. Rubber crumb should be added first with resins, plasticizers and fillers added in increments which do not disrupt the mixer action. Stabilizers should be introduced before the crumb receives appreciable shearing action in any case. Presoaking plasticizers into the thermoplastic crumb will speed mixing.

**Continuous Mixing Equipment.** Where production rates are high enough, continuous mixers are desirable since they reduce degradation of the rubbery midblock by excluding air and shorten residence time. Single-screw extruders often do not give adequate mixing. Twin-screw mixing extruders are much more

effective. Some of the newer continuous mixer designs are also very effective.<sup>a</sup>

### High Shear Melt Mixing Precautions.

Thermoplastic rubbers, particularly those with the highest melt viscosities, may build up excessive temperatures in high shear internal mixers (e.g., Banbury mixers<sup>b</sup>) if exposed to the high shear conditions in the absence of plasticizers and stabilizers. Certain precautions should be noted. While mass temperatures up to 400°F (425°F maximum) are normal in the mixing of thermoplastic rubber formulations, higher temperatures indicate too high a melt viscosity or too vigorous a mixing action. If the temperature were allowed to rise uncontrolled in such a situation (to 500°F and above), vaporization of plasticizer light ends and polymer decomposition could occur creating a potential fire hazard. Excessive temperatures can be avoided during the mixing operation by adding a resin or plasticizer or by reducing mixer speed. It is often desirable to investigate the mixing characteristics of a new composition on a small scale before undertaking large scale runs.

**Application Equipment.** Depending on melt viscosity and on the nature of the adhesive applications, various types of equipment are available. These include: pressure nozzle, print wheel, doctor blade, calender, die-coater, fountain coater, and extrusion coater. Where high strength, high viscosity products are involved, equipment is now available with closed or pressurized melting zones plus screw feed to the point of application. Applicators using strands of adhesive fed to a melt zone just before application are also suitable.

### Cooling and Remelting of Formulated Adhesives.

Provision is often made for cooling, storage, and remelting of adhesives between mixing and use. Since thermal conductivity of thermoplastic rubber is lower than that of EVA and polyolefins, thick layers of melted adhesive cool slowly, and if exposed to

air, may degrade. Cooling in thin cross sections is thus desirable. Because of the low heat conductivity and high viscosity at zero shear conditions, remelting should involve oil heaters to prevent surface overheating and a source of pressure to cause the adhesive to flow past the heating surface as melting occurs. Grid melters or "melt-on-demand" equipment are useful in this respect.

### Emulsions

Formulations based on thermoplastic rubbers can be made into emulsions by dispersing solutions or melts into water containing appropriate surface active agents. Normally, any organic solvent present would be stripped from the emulsion. High shear devices, such as colloid mills or centrifugal pumps, have been successfully used for the emulsifying step.

Compounding prior to emulsification enables resin and plasticizers to be distributed in an equilibrium manner between the thermoplastic rubber phases as in the adhesives discussed earlier. If the neat or plasticized thermoplastic rubber is emulsified alone and then mixed with a resin emulsion, the thermoplastic rubber will act only as a binder for the resin in the finished product.

Dried films are not likely to be continuous in either case. Dried films do not tend to coalesce unless heated above the  $T_g$  of the endblock domains. Heating causes the endblock domains to soften which allows the individual particles deposited from the emulsion to coalesce. Continuous films are not always necessary for adequate performance, and endblock coalescence is not needed in these cases.

### Powders

Mechanical size reduction of the thermoplastic rubber crumb can be accomplished using commercial rotating blade plastic granulators. Particle sizes down to at least 40-mesh can be produced without loss in tensile properties. However, as adjustments are made to produce progressively smaller particle sizes, throughput drops rapidly and cooling may be needed to prevent agglomeration of the small particles. Reagglomeration of the small particles may oc-

<sup>a</sup>For example, Multipurpose Continuous Mixers, Baker Perkins Inc.

<sup>b</sup>Farrel Co., Div. of USM Corp.

cur on long-time storage unless inorganic fillers or antiblocking agents are added to the powder.

Nonblocking powdered thermoplastic rubber can be made through the use of a special solvent system. In this method, rubber crumb is dispersed in a high solubility parameter solvent which will barely dissolve the endblock domains and which will not dissolve the rubber phase at all. One such single solvent is acetone. Particle size of the crumb is controlled by the amount of shear used in dispersion. Addition of water totally precipitates the small particles. This powder may then be separated from the liquid and dried. The particles do not tend to agglomerate because the hard endblock phase preferentially coats the outside of each particle.

### PROTECTION AGAINST DEGRADATION

Thermoplastic rubber with polydiene rubber midblocks is subject to chemical attack at the carbon-carbon double bonds (as are NR and SBR) and requires protection appropriate to the environment. Chain scission and crosslinking proceed simultaneously. In S-I-S polymers, scission predominates, and aging usually tends toward softening, stickiness, decrease in cohesive strength, and decrease in melt viscosity. In S-B-S polymers, on the other hand, crosslinking predominates and aging usually tends toward hardening, lower cohesive strength, increasing viscosity, and gel formation. In formulated products, both S-I-S and S-B-S polymers may tend to harden. In solutions, both may show viscosity decreases during aging.

#### Protection During Use

In formulated adhesives the resins, plasticizers, other polymers, etc., present must be protected as well as the thermoplastic rubber. Even hydrogenated rosin esters, polyterpenes, and olefinic hydrocarbon resins are reactive and must be protected.

The most appropriate stabilizer combination will depend on the selection of other formulation ingredients, as well as on the accelerated aging test conditions, and on the properties selected as indexes of product stability.

**Protection Against Oxygen Attack at Moderate Temperatures.** The rate of ox-

ygen attack on neat thermoplastic films, as measured by decrease in tensile strength and by degree of scission or crosslinking upon heating in air at 158°F, is greatly reduced by a number of commercial rubber stabilizers. The list in Table 6 is roughly in order of decreasing effectiveness with S-B-S or S-I-S thermoplastic rubber.

The addition of tackifying and other resins, even those which have been hydrogenated or otherwise stabilized, greatly increasing the rate of oxygen attack on thermoplastic rubbers.<sup>a</sup> The first four stabilizers listed in Table 6 alone or blended with others on the list, have been found to be effective for resin-containing formulations.

Accelerated aging tests in which pressure-sensitive adhesives are directly exposed to circulating air show much greater effects on the surface than in the film as a whole. Tests in which the surface is covered by a release paper show less oxidation and are more representative of conditions in rolled tapes or label stock.

Oxygen bomb testing (exposure to pure oxygen at 300 psig and 158°F) is often used in the evaluation of construction and other types of adhesives required to perform for periods of many years. Formulated S-B-S thermoplastic rubber films stabilized with 2 to 5 phr of antioxidants selected from Table 6 have retained flexibility for more than 1,000 hr in the oxygen bomb.

**Protection Against Ozone Attack.** Thermoplastic rubber with diene rubber midblocks is subject to attack by ozone when stressed. Antiozonants found to be useful include NBC,<sup>b</sup> Pennzone B,<sup>c</sup> and Ozone Protector 80.<sup>d</sup>

**Protection During Exposure to Ultraviolet Radiation.** Commercially available ultravi-

<sup>a</sup>Tack loss occurring during aging of pressure-sensitive adhesives has been traced in some cases to the hydration of ester-type resins in the formulation. Therefore, in case of a tack loss problem, it should be determined whether the loss is oxidative or due to moisture pickup. Where hydration occurs, control of water pickup during manufacture or storage, change in resin type, or the removal of the moisture in a vacuum oven are possible solutions.

<sup>b</sup>Nickel dibutylthiocarbamate (E. I. duPont deNemours & Co.).

<sup>c</sup>Dibutylthiourea (Pennwalt Corp.).

<sup>d</sup>Reichhold Chemicals, Inc.



**Table 6. Antioxidants for Thermoplastic Rubbers.**

<i>Trade Name</i>	<i>Chemical Type</i>	<i>Supplier</i>	<i>Starting Level, phr</i>
Irganox® 1010	Tetra- <i>bis</i> -methylene-3-(3,5-di- <i>tert</i> -butyl-4-hydroxyphenyl) propionate methane	Ciba-Geigy	0.3–2
Antioxidant 330® Irganox 1330	1,3,5-trimethyl-2,4,6- <i>tris</i> (3,5-di- <i>tert</i> -butyl-4-hydroxybenzyl) benzene	Ethyl Corp. Ciba-Geigy	0.3–2
Cyanox® 2246 <sup>a</sup> Vanox® 2246 <sup>a</sup>	2,2-methylene- <i>bis</i> (4-methyl-6- <i>tert</i> -butyl phenol)	American Cyanamid R. T. Vanderbilt	0.5–2
Cyanox 425 <sup>a</sup>	2,2-methylene- <i>bis</i> (4-ethyl-6- <i>tert</i> -butyl phenol)	American Cyanamid	0.5–2
Santowhite® Crystals Irganox 565	4,4-thio- <i>bis</i> -(6- <i>tert</i> -butyl- <i>m</i> -cresol) 2(4-hydroxy-3,5- <i>tert</i> -butylanilino)-4,6- <i>bis</i> ( <i>n</i> -octylthio)-1,3,5-triazine	Monsanto Co. Ciba-Geigy	1–2 0.5–2
Polygard® <sup>b</sup> Butyl Zimate® Butazate® Butasan® Butyl Ziram®	Tri(nonylated phenyl) phosphite Zinc dibutyl dithiocarbamate	Uniroyal Chem. R. T. Vanderbilt Uniroyal Chem. Co. Monsanto Co. Pennwalt Co.	0.3–5 1–4

<sup>a</sup>May produce colored formulations.<sup>b</sup>Polygard may be useful at high temperatures (150–200°C).

olet stabilizers are effective in thermoplastic rubber formulations. Table 7 is a list of such with the more effective at the beginning.

In opaque products, the addition of a reflective filler such as zinc oxide or titanium dioxide<sup>a</sup> or a light absorber such as carbon black<sup>b</sup> may provide satisfactory protection.

Oils containing small amounts of aromatic compounds are particularly unstable with regard to ultraviolet radiation. The use of aromatic free “white oils” in thermoplastic rubber

formulations will improve ultraviolet resistance markedly.

### Protection During Processing

**Protection During Hot-Melt Mixing.** Exclusion of oxygen during high shear mixing at 250–400°F has been found to be an effective means to prevent polymer degradation. Figure 16 shows that no change in melt viscosity occurs during high shear mixing when the mixer is nitrogen blanketed. With oxygen present and distributed throughout the mixture significant viscosity changes result at increasing rotor

<sup>a</sup>For example: Titanox RA-50 (Titanium Pigment Corp.).<sup>b</sup>For example: Fast extrusion furnace (FEF) blacks.**Table 7. UV Inhibitors for Thermoplastic Rubbers.**

<i>Trade Name</i>	<i>Chemical Type</i>	<i>Supplier</i>
Eastman OPS	Octylphenyl salicylate	Eastman
Eastman RMB	Resorcinol monobenzoate	Eastman
Permasord MA	2-hydroxy-4-(2-hydroxy-3-methacryloxy) propiobenzo-phenone	National Starch
Tinuvin P	Substituted benzotriazole	Ciba-Geigy
Tinuvin 326	Substituted hydroxyphenyl benzotriazole	Ciba-Geigy
Tinuvin 770	Hindered amine	Ciba-Geigy
Antioxidant 330	1,3,5-trimethyl-2,4,6- <i>tris</i> (3,5-di- <i>tert</i> -butyl-4-hydroxybenzyl) benzene	Ethyl Corp.
Irganox 1076	Octadecyl-3-(3,5-di- <i>tert</i> -butyl-4-hydroxyphenyl) propionate	Ciba-Geigy
Irganox 1010	Tetra- <i>bis</i> -methylene-3-(3,5-di- <i>tert</i> -butyl-4-hydroxyphenyl)propionate methane	Ciba-Geigy

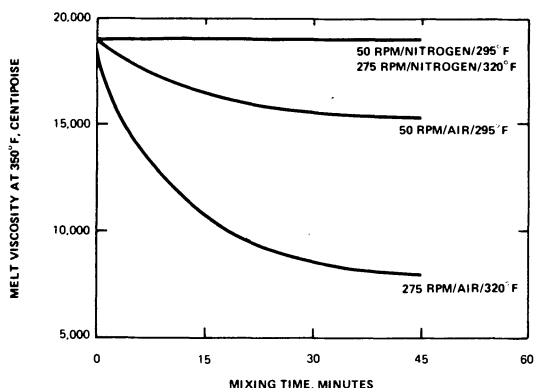


Fig. 16. Effect on melt viscosity of oxygen contact during high shear mixing of a pressure sensitive adhesive based on an S-I-S thermoplastic rubber.

speeds. Degradation can also be reduced by the use of certain stabilizers (e.g., zinc dibutyldithiocarbamate at levels of 1–5 phr).

Contact with air is greatest in open stirred vessels and least in closed sigma-blade mixers. The data in Fig. 16 show that, in the absence of oxygen, moderate temperatures and mechanical shear are not major causes of degradation.

#### Protection During Solution Processing.

Adequate protection during solution mixing, application to the substrate, solvent evaporation, and storage of thermoplastic rubber formulations can be provided by a combination of the chemical stabilizers listed in Table 6. A high temperature drying step for solvent evaporation may require special consideration, but degradation is not usually a problem in such a case due to the short exposure times involved.

### FORMULATING FOR SPECIFIC APPLICATIONS

In general, each new adhesive product must meet a definite set of performance specifications and must fall within certain manufacturing cost limitations. How is a thermoplastic rubber formulation developed to match such requirements? One effective approach is outlined below:

1. Select one or two thermoplastic rubbers based on manufacturer's suggestions or on previous experience.

2. Select a starting formulation in the same way.
3. Prepare a series of formulations based on related resins, plasticizers, fillers, etc., using simplified solution casting methods, and measure the important properties of the product.
4. Using these results and the principles illustrated below, optimize the balance between the various properties including raw material cost.
5. Prepare samples by the actual manufacturing process to confirm the results of the screening program.

### Some Formulating Principles

The characteristics of formulations based on thermoplastic rubber depend, as already discussed, on how the various compounding ingredients interact with the two phases present. The following generalizations, although they may not be valid for all compositions, provide useful clues which can guide formulation development studies.

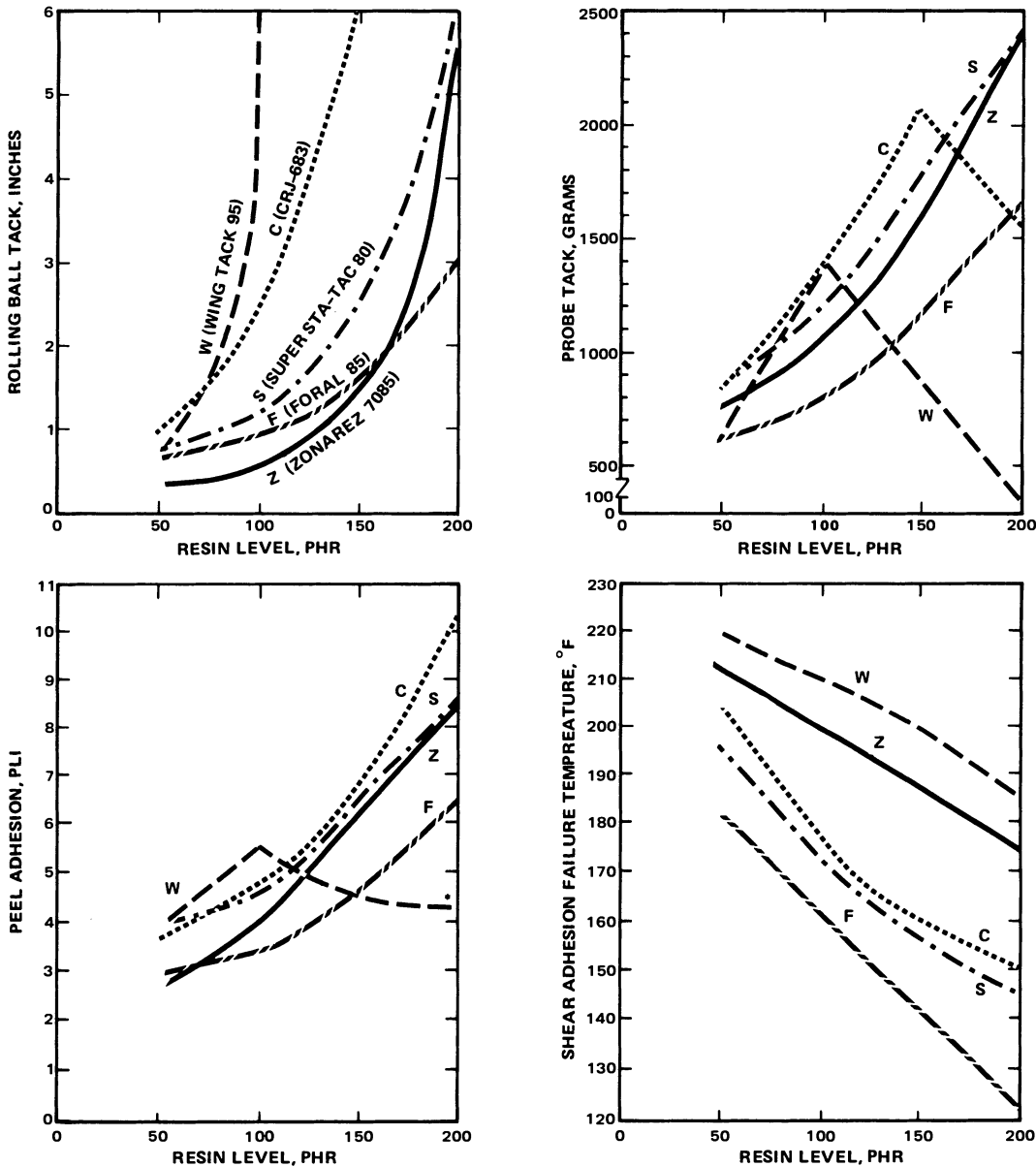
1. Endblock resins may either raise or lower the upper service temperature limit. Midblock resins will raise and midblock plasticizers may decrease the lower temperature limit.
2. Midblock resins and plasticizers tend to lower the modulus and soften formulations by decreasing the concentration of hard endblock phase; endblock resins tend to raise the modulus for the reverse reason.
3. Pressure-sensitive tack tends to be favored by polyisoprene midblocks over polybutadiene midblocks; such tack is produced by some midblock resins and not by others; all solid endblock resins tend to lower pressure-sensitive tack by increasing modulus; rubber phase plasticizers tend to increase aggressive tack by lowering modulus.
4. Peel strengths tend to increase with increasing formulation modulus; specific adhesion to polar or metal substrates tends to be increased by polar, unsaturated, or aromatic resins and to be decreased by hydrocarbon plasticizers.

5. Melt and solution viscosities tend to be markedly decreased by both resins and plasticizers; inorganic fillers will tend to increase viscosity.

Other guiding principles can be established by experience and by considering a given application in the light of background information already presented in this chapter.

**A Condensed Case Study—Formulating a Hot-Melt Pressure-Sensitive Adhesive**

Binary mixtures of an S-I-S polymer (KRA-TON 1107) and a number of midblock resins were examined first. Solutions in a good solvent were cast to form 1 mil films on a 1 mil polyester film. After thorough drying, the film was tested for several properties. Figure 17



\*BRITTLE PEEL AT 200 PHR FOR C; AT 150 AND 200 PHR FOR W

Fig. 17. Effect of midblock resins (Table 4) on adhesive properties of two-component pressure sensitive adhesives (see Table 8).

shows how four properties varied with the level of five dissimilar resins. Because of its high shear adhesion failure temperature<sup>a</sup> and acceptable peel adhesion<sup>b</sup> and probe tack,<sup>c</sup> 100 phr WingTack 95 was selected for further work. (See first column, Table 8.)

More aggressive tack was desired, so a plasticizer was added. Shellflex 371 oil was selected from Table 5 because of its good compatibility with the midblock phase (i.e., low bleedout tendency) and low cost. The data in Table 9 show the effect of adding increasing amounts of oil.

Addition of the plasticizer caused a loss in

Shear Adhesion Failure Temperature, peel adhesion, and holding power. To restore these properties, high softening point endblock resins were added. Figure 18 summarizes the effects of four such resins in the formulation containing 25 parts of oil (Table 9). Cumar LX-509 resin was selected for use in a final formulation because it had the greatest beneficial effect on shear adhesion failure temperature and showed only moderate loss in rolling ball tack.

The final four component composition is compared in Table 8 with the intermediate two and three component formulations. The final composition combines the same Shear Adhesion Failure Temperature as the first with much more aggressive tack, a much lower melt viscosity (for low-cost application), and lower raw materials cost. This set of properties or any other set of properties can be obtained in more than one way. Given a growing background of

<sup>a</sup>Test method described previously.

<sup>b</sup>Pressure-Sensitive Tape Council (PSTC) Test Methods, Ref. 28.

<sup>c</sup>Probe Tack: Determined by a Polyken Probe Tack Tester (Testing Machines, Inc.) Conditions: 1 cm/sec Speed, 1 sec dwell, 100 gm/cm<sup>2</sup> pressure.

**Table 8. Hot-Melt Pressure-Sensitive Adhesive Based on S-I-S.**

	Two Components, (parts)	Three Components, (parts)	Four Components, (parts)
S-I-S (Kraton 1107 Rubber):	100	100	100
Midblock resin (Wingtack 95):	100	100	100
Plasticizing oil (Shellflex 371):	—	40	40
Endblock resin (Cumar LX-509):	—	—	60
Stabilizer (zinc dibutyldithio-carbamate):	5	5	5
<b>TOTAL</b>	<b>205</b>	<b>245</b>	<b>305</b>
Shear adhesion failure temp., °F	210	188	220
Rolling ball tack (PSTC-6), cm	5.9	0.6	1.8
Probe tack, gm	1300	700	1100
180° peel adhesion (PSTC-1), pli	5.3	2.5	3.7
Melt viscosity at 350°F, cp	200,000	30,000	40,000
Holding Power to Kraft paper, min.	>2800	5	150
Thermoplastic rubber content, %w	49	38	33

**Table 9. Effect of Plasticizing Oil on Adhesive Properties.**

Oil Level, phr:	0	25	40	60
Shear adhesion failure temperature, °F	218	192	188	177
Rolling ball tack (PSTC-6), cm.	5.6	0.9	0.6	0.7
Probe tack, gm	1600	1000	700	600
Peel Adhesion (PSTC-1), pli	5.5	3.6	2.5	1.8
Melt Viscosity (350°F), cp	200,000	100,000	30,000	20,000
Holding Power to Kraft paper (PSTC-7), minutes	>2800	100	5	<1

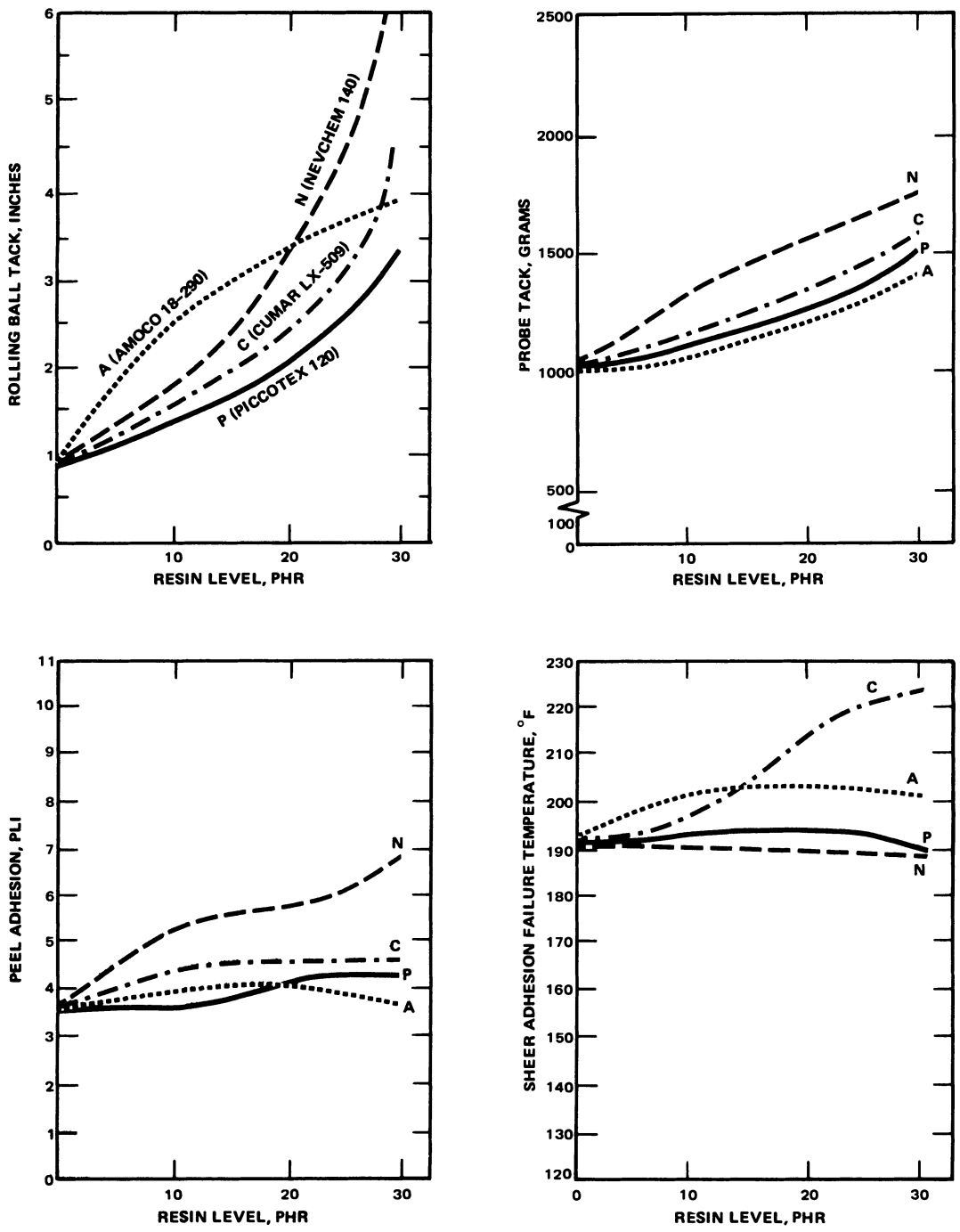


Fig. 18. Effect of endblock resins (Table 3) on adhesive properties of Kraton 1107 (100 parts), Wingtack 95 (100 parts), and oil (25 parts) (see Table 9).

property data and an understanding of the versatility of thermoplastic rubber, the formulator has a broad range of tailored products at hand.

### Starting Formulations

**Pressure Sensitive Adhesive Based on S-B-S.** The formulation shown in Table 10 has high holding power, but little aggressive tack. However, as in the case study above, all properties including Rolling Ball Tack can be adjusted by adding plasticizing oil (e.g., Tufflo 6054) or by varying type and amounts of resins.

**Improving the Strength of General Purpose Rubber Formulations.** The Shear Adhesion of natural rubber or SBR masscoats can be improved by the addition of thermoplastic rubber as shown in Table 11. S-I-S polymers are most compatible with natural rubber, and S-B-S polymers are most compatible

with SBR. However, S-B-S/natural rubber and S-I-S/SBR blends may also be useful if some turbidity can be tolerated.

### Hot Melt Applied Assembly Adhesive.

Table 12 describes an assembly adhesive based on an S-B-S polymer. A different combination of properties can be obtained by using an S-I-S base polymer. Several useful features may result from the use of S-I-S: (a) generally better clarity, (b) lower melt viscosities, and (c) freedom from gel formation which can occur when S-B-S formulations are exposed to oxygen at high mixing and application temperatures.

**Heat-Activated Assembly Adhesive.** Table 13 describes a solution adhesive which can be coated on two substrates, dried, activated by heating both surfaces to 165°F, and bonded by pressing the substrates together. The adhesive is nonblocking at room temperature.

**Table 10. Pressure-Sensitive Adhesive Based on S-B-S.**

Composition (wt. parts)	
S-B-S (Kraton 1101 Rubber)	100
Midblock resin (Super Sta-Tac 80)	200
Stabilizer	1
Properties	
Rolling ball tack (PSTC-6), in.	10
Probe tack, gm	1700
180° Peel Adhesion, (PSTC-1), pli	7.6
Shear adhesion failure temperature, °F	180
Thermoplastic rubber content, %w	33
Endblock/Midblock Ratio	10/90

**Contact Type Assembly Adhesive.** Modifying the above formulation to include equal parts of midblock and endblock resins with high softening points gives the contact adhesive shown in Table 14. Essentially nontacky to most surfaces, this type of adhesive bonds strongly to itself after open times of several minutes to a few hours when cast from a hexane/toluene/acetone solvent system in the ratio 60/20/20.

The development of film-to-film adhesion (canvas/canvas peel strength, ASTM-D-1876) with bonding after 30 min open time is shown in Fig. 19 for the two formulations given in Table 15.

**Table 11. Pressure-Sensitive Adhesive – Effect of S-B-S on Shear Strength.**

Composition (wt. parts)		
SBR (S-1006, ML-50)	100.0	75.0
S-B-S (KRATON 1101 Rubber)	—	25.0
Midblock Resin (Foral 85)	100.0	100.0
Stabilizer (Irganox 1010/DLTD = 1/1)	0.6	0.6
Properties		
Shear adhesion to glass (PSTC-7), hr	0.1	1.0
180° peel adhesion (PSTC-1), pli	1.1	0.9
Rolling ball tack, (PSTC-6), in.	4	4

**Table 12. Hot-Melt Applied Assembly Adhesive.**

Composition (wt. parts)	
S-B-S (Kraton 1102 Rubber)	100
Endblock resin (Piccotex 120)	150
Midblock resin (Wingtack 115)	50
Plasticizing oil (SHELLFLEX 371)	50
Stabilizer	2-5
Properties	
Melt viscosity at 350°F	16,000 cp
Tensile strength, $T_B$	600 psi (draws)
Elongation, $E_B$	700%
Shore A Hardness	90
Lap Shear (Plywood/plywood)	214 psi
Flexibility at 0°F	Good
Shear adhesion failure	
Temperature	163°F
Endblock/midblock ratio	51/49

**Table 13. Heat Activated Adhesive.**

Composition (wt. parts)	
S-B-S (Kraton 1101 Rubber)	100
Endblock resin (Cumar R-16)	75
Low molecular weight Endblock resin (Piccovar AP-25)	25
Stabilizer (Antioxidant 330/DLTDP = 1/1)	0.6
Solvents	
Toluene	120
Cyclohexane	120
Methyl ethyl ketone	60
Properties	
Peel adhesion (PSTC-1), pli	50
Creep (180° Peel at 140°F, 3 pli load), in/10 min.	0.2
Endblock/Midblock ratio	65/35

**Reactive Contact Adhesives.** The heat resistance of contact adhesives can be increased by using curing phenolic resin systems. Table 16 compares two formulations, one with and one without a reactive resin system.

**Building Construction Adhesive.** The starting composition of Table 17, suitably formulated with solvents, is a high strength adhesive which can be used for factory or field assembly of housing components. With stabilizer systems similar to that shown, oxygen bomb aging exceeds current building requirements.

**Table 14. Contact Type Assembly Adhesive.**

Composition (parts by wt.)	
S-B-S (KRATON 1101 Rubber)	100
Endblock resin (PICCO N-100)	37.5
Midblock resin (Pentalyn H)	37.5
Stabilizer (Antioxidant 330)	0.6
Properties: (30 min. open time, no heat or solvent activation) 180° Peel Strength (PSTC-1), pli	
Canvas/fir plywood	14
Canvas/stainless steel	14
Canvas/vinyl asbestos floor tile	9
Lap shear strength (0.5 in./min. Instron crosshead speed)	137
Endblock/Midblock ratio	39/61

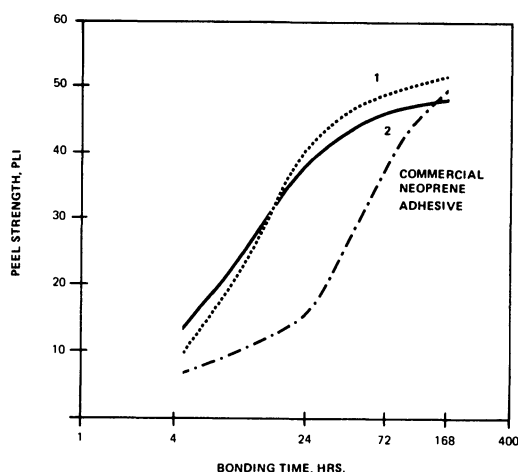


Fig. 19. Development of contact adhesive bond strength.

**Table 15. Contact Adhesives.**

Composition (wt. parts)	1	2
S-B-S (Solprene 406 Rubber)	100	—
S-B-S (Solprene 411 Rubber)	—	100
Endblock resin (PICCO 6115)	40	40
Midblock resin (Pentalyn H)	10	10
Solvents		
Hexane	150	150
Acetone	150	150
Toluene	150	150

**Wax-Containing Hot-Melt Assembly Adhesive.** Blends of paraffin wax, S-B-S, and a compatibilizing resin may be used for bonding paper, textiles, etc as shown in Table 18.

**Table 16. Contact Adhesive – Effect of Heat Reactive Resin.**

Composition (wt. parts)	Nonreactive Resin	Reactive Resin
S-B-S (Solprene 411 Rubber)	100	100
Reactive resin (Schenectady SP-154)	—	45
Endblock resin (PICCO 6115)	40	—
Midblock resin (Pentalyn H)	10	—
Magnesium oxide	—	8.6
Zinc oxide	—	5.0
Stabilizer	1	1
Solvents		
Hexane	150	127
Acetone	150	127
Toluene	150	127
Properties		
Peel strength (canvas/canvas), pli	48	25
Peel adhesion failure temperature (canvas/canvas, 0.22 pli; 40°F/hr), °F	176	230

**Table 17. High Viscosity Construction Mastic.**

Composition (wt. parts)	
S-B-S (Kraton 1101)	100
Endblock resin (PICCO N-100)	75
Soft clay	200
Stabilizers	
Zinc dibutylthiocarbamate	2
Plastanox 2246	1
Properties	
Lap shear strength (Wood/wood, 0.5 in./min crosshead speed), psi	590

**Table 18. Hot-Melt Assembly Adhesive.**

Composition (wt. parts)	
S-B-S (Kraton 1102 Rubber)	100
Midblock resin (Super Sta-Tac 100)	100
Paraffin wax (Shellwax 300)	85
Stabilizer	1
Properties	
Peel strength (canvas/canvas), pli	45

In this case, the wax functions in the same way as the plasticizing oils discussed above.

**Sealants.** Sealants often require only gap-filling characteristics. Such products are generally low modulus compounds which readily

**Table 19. Sealant for Concrete Joints.**

Composition (wt. parts)	
S-B-S (Kraton 1101 Rubber)	100.0
Asphalt 250 dmm pen, 233 poise @ 140°F)	180.0
Plasticizing oil (Shellflex 881)	60.0
Midblock resin (Picco LTP-100)	60.0
Stabilizers	1.0
Properties	
Penetration at 77°F, dmm	86
Resilience at 77°F, %	83
Flow at 140°F, in.	0
Viscosity at 400°F, cps	2060
Softening point R&B, °F	218

expand and contract without losing adhesion. In some applications, however, stress is carried by the sealant such that the material is effectively an adhesive-sealant. Thermoplastic rubber polymers can be formulated to meet the requirements of either kind of sealant. A concrete/concrete sealant is shown in Table 19.

**Binders.** Binders should be elastic while still maintaining strong adhesion to the substance being bound. The resulting product can be soft and flexible as in a carpet backing or stiff and hard as in an abrasive. Thermoplastic rubber has the capacity for great extension, particularly with inert fillers. An example of a flexible carpet backing is shown in Table 20.



**Table 20. Binder for Carpet Backing.**

Composition (wt. parts)	
S-B-S (Kraton 1101 Rubber)	100
Plasticizing oil (Shellflex 371)	150
Whiting	700
Stabilizer	1
Properties	
Hardness, Shore A	55
Specific gravity	1.8

## PERMANENT CROSSLINKING

Pressure sensitive adhesives based on thermoplastic rubbers perform well over the temperature range required in the majority of pressure sensitive product applications. However, as the temperature at which the product will be used approaches the glass transition temperature of the endblock phase of the rubber (usually about 92°C), the polystyrene endblock domains begin to soften and unlock the physical crosslinks. When this occurs, the rubber midblocks are no longer crosslinked and the adhesive shows a drastic reduction in cohesive strength. Therefore adhesives based on thermoplastic rubber cannot be used, for example, on high temperature masking tapes, which must have some solvent resistance and withstand a significant load at temperatures in paint baking ovens of up to 170°C. This limitation can be overcome by crosslinking the rubber in the adhesive so that it will no longer be thermoplastic.

The double bonds in the midblocks of the unsaturated S-B-S and S-I-S polymers provide the sites for crosslinks. These unsaturated thermoplastic rubbers can be crosslinked with the usual sulfur, sulfur donor, or peroxide curing systems traditionally used for crosslinking unsaturated rubbers. There are many combinations of ingredients which could be used in a sulfur based crosslinking package. For example, the crosslinking package could contain 0.3–1.5 phr of elemental sulfur or a sulfur donor (e.g., Sulfads, dipentamethylene thiuran hexasulfide, Vanderbilt), 0.3–1 phr of an accelerator (e.g., Altax, benzothiazyl disulfide, Vanderbilt or Methyl Zymate, zinc dimethyldithiocarbamate, Vanderbilt), and 0.3–1 phr of zinc oxide and stearic acid. A peroxide cross-

linking system could contain 1–4 phr of peroxide (e.g., DI CUP, dicumyl peroxide, Hercules), and could be used in combination with 5.25 phr of a reactive acrylic monomer (e.g., Sartomer SR 351, an acrylic monomer, Sartomer Corp.). Either the sulfur or the peroxide crosslinking package can be mixed directly into the adhesive solution, and crosslinking occurs thermally as the adhesive tape passes through the solvent evaporation ovens.

Another approach to improve the high temperature cohesive strength of adhesives based on thermoplastic rubber is by establishment of a thermoset network extending throughout the rubber phase. This can be accomplished by the use of reactive phenolic resins in combination with a metal catalyst. An example of a formulation which is claimed to be effective is given in Table 21. This type of crosslinking system can be mixed directly into the adhesive solution and crosslinking is initiated thermally in the solvent evaporation ovens.

A thermally initiated crosslinking reaction would almost always be used to crosslink an adhesive applied from solvent because crosslinking can be conveniently initiated in the solvent evaporation ovens. However, thermally initiated crosslinking systems present considerable handling problems for hot melt adhesives in that they may crosslink the adhesive in the hot melt processing equipment.

A crosslinking system which can be initiated by exposure to radiation is a more practical route to crosslink a hot melt adhesive. The for-

**Table 21. Pressure Sensitive Adhesive Crosslinked with Phenolic Resin.**

Parts by Weight	
S-I-S Polymer <sup>a</sup>	100
C <sub>5</sub> resin <sup>b</sup>	50
Phenol-formaldehyde resin <sup>c</sup>	20
Zinc resinate <sup>d</sup>	10
Zinc dibutyldithiocarbamate	2
2,5-di- <i>tert</i> -amylhydroquinone <sup>e</sup>	1
%w solids in toluene	50

<sup>a</sup>Kraton® D1107 Rubber; Shell.

<sup>b</sup>Wingtack® 95; Goodyear.

<sup>c</sup>Amberol ST-137; Rohm and Haas.

<sup>d</sup>Reichhold.

<sup>e</sup>Santovar® A; Monsanto.

mulations shown in Table 22 can be crosslinked by exposure to ultraviolet (UV) radiation. The reactive monomer, SR-351 (trimethylolpropane triacrylate), is used in the formulation to reduce the radiation dose required to achieve crosslinking of the adhesive. In addition, a photoinitiator, Irgacure® 651, is needed to generate free radicals by dissociating rapidly under UV exposure, which initiate the crosslinking reaction. Both adhesive formulations in Table 22 tend to crosslink when held at hot melt processing temperatures. However, both adhesives crosslink slowly enough that they can be extrusion coated onto the tape substrate before significant crosslinking has occurred. The formulations can be crosslinked by exposure, under a nitrogen blanket, to ultraviolet light by passing the adhesive under a high pressure mercury lamp. However, it is required that the light be filtered to remove the portion of the spectrum whose wavelength is less than 310 nanometers in order to prevent degradation of the surface of the adhesive. Formulation A,

in Table 22 is based on a conventional S-I-S polymer and requires a belt speed of 3.0 m/min to obtain sufficient crosslinking. Formulation B, on the other hand, is based on a new (S-I)<sub>n</sub> radial block polymer, Kraton® D1320X Rubber, designed for crosslinked adhesives and obtains sufficient crosslinking at a belt speed of 12.0 m/min.

Adhesives can also be crosslinked by exposure, under a nitrogen blanket, to electron beam (EB) radiation at a dose of 1 to 10 megarads. Table 23 demonstrates the effectiveness of Kraton® D1320X Rubber, Formulation B, in obtaining a crosslink network at 5 megarads *without* the use of a reactive monomer. Formulation A is based on a typical S-I-S polymer and shows a lack of crosslinking at the 5 megarad dose. Electron beam crosslinking of typical S-I-S polymers require the addition of reactive monomers and usually higher EB doses.

Because their midblock is saturated, the S-EB-S and S-EP-S polymers are much more

**Table 22. Pressure Sensitive Adhesive Formulations Crosslinked by Exposure to UV Radiation.**

	Formulation	
	A	B
S-I-S polymer <sup>a</sup>	100	—
Kraton® D1320X rubber <sup>b</sup>	—	100
Wingtack® 95 <sup>c</sup>	80	80
TMPTA <sup>d</sup>	7.5	7.5
Irgacure® 651 <sup>e</sup>	1.0	1.0

	Adhesive Properties			
	A		B	
	Before UV Cure	After UV Cure	Before UV Cure	After UV Cure
Belt speed, m/min	—	3.0	—	12.0
Gelcontent, % <sup>f</sup>	0	92	0	89
Rolling ball tack, cm	1.4	14.3	2.8	4.1
Polyken® probe tack, kg	0.9	0.8	1.0	0.9
180° peel, N/m	720	530	630	540
Holding power to steel, hr <sup>g</sup>	> 70	> 44	> 88	> 88
Holding power to kraft, hr <sup>g</sup>	> 70	0.3	> 88	> 88
70°C holding power to kraft, hr <sup>h</sup>	1.5	0.5	5	27

<sup>a</sup>KRATON® D1107 Rubber; Shell Chemical.

<sup>b</sup>Shell Chemical.

<sup>c</sup>Goodyear.

<sup>d</sup>Trimethylolpropane triacrylate, SR-351; Sartomer.

<sup>e</sup>Ciba-Geigy.

<sup>f</sup>Percent polymer fraction not soluble in toluene.

<sup>g</sup>12.7 × 12.7 cm with 2 kg load.

<sup>h</sup>25.4 × 25.4 cm with 1 kg load.

**Table 23. Pressure Sensitive Adhesive Formulations Crosslinked with Electron Beam Radiation.**

	<i>Formulation</i>			
	<i>A</i>		<i>B</i>	
S-I-S polymer <sup>a</sup>	100.0		—	
Kraton® D1320X rubber <sup>b</sup>	—		100.0	
Wingtack® 95 <sup>c</sup>	88.9		88.9	
Adtac® B10 <sup>d</sup>	11.1		11.1	
Antioxidant 330 <sup>®e</sup>	0.4		0.4	
BHT	0.3		0.3	

	<i>Adhesive Properties</i>			
	<i>A</i>		<i>B</i>	
E.B. Dose, Mrad	0	5	0	5
Gel content, % <sup>f</sup>	0	0	0	90
Rolling ball tack, cm	1.4	3.4	1.2	1.8
Polyken® probe tack, kg	1.3	1.4	1.2	1.4
180° peel, N/m	1050	930	875	980
Holding power to steel, hr <sup>g</sup>	>67	>67	>67	60
Holding power to kraft, hr <sup>g</sup>	63	>67	60	>67
95°C holding power to Mylar, hr <sup>h</sup>	2.0	2.1	1.9	>17

<sup>a</sup>Kraton® D1107 Rubber; Shell Chemical.<sup>b</sup>Shell Chemical.<sup>c</sup>Goodyear.<sup>d</sup>Hercules.<sup>e</sup>Ethyl Corp.<sup>f</sup>Percent polymer fraction not soluble in toluene.<sup>g</sup>12.7 × 12.7 cm with 2 kg load.<sup>h</sup>25.4 × 25.4 cm with 1 kg load.

difficult to crosslink. A formulation similar to the formulations in Table 22, with a reactive monomer, containing an S-EB-S polymer rather than an S-I-S polymer cannot be crosslinked at commercially acceptable rates by exposure to ultraviolet light. It can be crosslinked by exposure to electron beam radiation, but doses of at least 6 megarads are required.

Resins can also affect the rate of crosslinking on exposure to radiation. Table 24 demonstrates the effectiveness of hydrogenated resins, Sample No. 1, in obtaining a crosslink network in a formulation based on the (S-I)<sub>n</sub> polymer, Kraton® D1320X Rubber. At an electron beam dose of 1 megarad, Sample No. 1 has a gel content (that portion of the polymer that is not soluble in toluene) of 45% and an increase in high temperature performance (shear adhesion failure temperature, SAFT) of 30°C. At 3 megarads the gel content has increased to 90% and the holding power at 95°C (i.e., above the *T<sub>g</sub>* of the endblock) has increased to 11 hours. The unsaturated resins, Samples No. 2, 3 and 4, required much higher

electron beam doses to obtain a high gel content and an improvement in SAFT or 95°C holding power.

It must be noted that while crosslinking an adhesive based on a thermoplastic rubber brings about the desired improvement in high temperature cohesive strength and solvent resistance, it can also cause a reduction in aggressive tack of the adhesive. Unless the rubber has been designed specifically for use in crosslinked adhesives, chemical crosslinking of a thermoplastic rubber corresponds roughly to overcuring a conventional rubber vulcanizate.

## APPENDIX

### SOLUBILITY PARAMETER ( $\delta$ )—A POWERFUL TOOL

Hildebrand's solubility parameter ( $\delta$ ) has been used in the text to correlate the solubility behavior of thermoplastic rubber (e.g., Figs. 9–11). This parameter is potentially an extremely powerful tool for studying formulations based on two-phase thermoplastic rubber.

**Table 24. Effect of Resins on Electron Beam Crosslinking of (S-I)<sub>n</sub> Thermoplastic Rubber Pressure Sensitive Adhesives.**

ID No. <sup>a</sup>	EB Dose, Mrad	Gel Content, <sup>b</sup> %	Rolling Ball Tack, cm	Saft Mylar, <sup>c</sup> °C	95°C Holing Power, <sup>d</sup> min	180° Peel, N/m
<i>Escorez® 5380/Regalrez® 1018</i>						
1	0	0	1.7	74	6	540
	1	45	1.4	104	50	470
	3	90	1.6	112	670	470
	5	93	3.2	113	800	420
	7	95	4.0	114	1000+	390
<i>Wingtack® 95/Adtac® B10</i>						
2	0	0	2.5	92	23	840
	1	4	2.5	97	50	720
	3	69	1.9	115	165	720
	5	89	4.3	122	290	680
	7	95	4.3	114	500	700
<i>Wingtack 95/Wingtack 10</i>						
3	0	0	1.5	88	11	630
	1	0	1.3	93	26	610
	3	62	1.3	100	125	530
	5	77	3.0	116	130	600
	7	90	1.8	114	140	560
<i>Escorez 1310/Adtac B10</i>						
4	0	0	2.9	91	12	770
	1	3	1.8	96	33	770
	3	74	1.7	110	180	630
	5	75	3.1	111	190	650
	7	82	4.6	115	650	670

*Formulations:	1	2	3	4
Kraton® D1320X Rubber; Shell	100.0	100.0	100.0	100.0
Escorez 5380; Exxon	60.8	—	—	—
Regalrez 1018; Hercules	61.4	—	—	—
Wingtack 95; Goodyear	—	69.4	50.1	—
Escorez 1310; Exxon	—	—	—	74.2
Adtac B10; Hercules	—	52.8	—	48.0
Wingtack 10; Goodyear	—	—	72.1	—
Antioxidant 330®; Ethyl Corp.	0.4	0.4	0.4	0.4
BHT	0.3	0.3	0.3	0.3

<sup>b</sup>Percent polymer fraction not soluble in toluene.<sup>c</sup>25.4 × 25.4 cm with 1 kg load, temperature at failure of adhesive bond.<sup>d</sup>25.4 × 25.4 cm with 1 kg load.

It has an exact value for each compounding ingredient: solvent, polymer, resin, plasticizer, stabilizer, etc. The distribution of any ingredient between the two polymer phases and its consequent effects on formulation behavior is usually a function of the values of  $\delta$  for the various components. Unfortunately, at present, values of  $\delta$  are readily available only for solvents, oils, and certain polymers. However, due to its usefulness, it is probable that in the near future  $\delta$  will be determined for more ma-

terials and better methods will be developed for applying it. This appendix is intended to clarify the significance of  $\delta$  and to point out its relationship to thermoplastic rubber compounding.

**Significance of  $\delta$ .** For two materials to be mutually soluble, the free energy of mixing must be negative. This situation is usually favored if the values of  $\delta$  for the two materials are close. In general, the higher the molecular weight of one or both materials is, the closer

must be the values of  $\delta$  for miscibility to occur. Thus, for example, if one knew the values of  $\delta$  and molecular weight for a series of resins, one might be able to select or design a resin which would optimize a certain property.

**Definition of  $\delta$** —Hildebrand<sup>18</sup> proposed the name “solubility parameter” for the following quantity:

$$\delta = (\text{cohesive energy density, CED})^{1/2}$$

$$\text{in (cal/cm}^3)^{1/2}$$

$$= \frac{E_v^{1/2}}{V_m}$$

where

$E_v$  = isothermal energy of vaporization into a vacuum, cal/mole

and  $V_m$  = molar volume, cm<sup>3</sup>/mole.

The units, (cal/cm<sup>3</sup>)<sup>1/2</sup>, have been designated as “hildebrands” in honor of the originator of the term solubility parameter.<sup>19</sup> As defined,  $\delta$  is a measure of the total intermolecular bond energy holding the molecules of a substance together. If the bonds holding the molecules of substance (1) together are much stronger than those holding substance (2) together (i.e.,  $\delta_1 > \delta_2$ ), each species of molecule will prefer its like neighbors and will refuse to mix with molecules of the other substance. Conversely, if  $\delta_1 = \delta_2$ , the molecules of (1) will tolerate the proximity of the molecules of (2), and vice versa. Many discussions and tabulations of solubility parameter have appeared in the literature; several of the more useful are included as references.<sup>18-27</sup>

**Simple Cases.** Nonpolar hydrocarbon solvents like cyclohexane and nonpolar polymers like polyisoprene follow the above rules, and correlations like that presented in Fig. 10 are quite precise. Here the intermolecular bonds are almost solely due to van der Waal's forces.

**Complex Cases.** Where molecules are appreciably polar in nature and where intermolecular hydrogen bonding is possible,  $\delta$  is no longer a simple number. In such a case,  $\delta$  is actually the sum of three different bond energy

components and must be represented as follows:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$

where

$\delta_d$  = bond energy due to van der Waal's forces,

$\delta_p$  = bond energy due to all polar interactions, and

$\delta_h$  = bond energy due to all hydrogen bonding interactions.

Thus,  $\delta$  is actually a three-dimensional quantity which could be represented as a point in three-dimensional space.<sup>19-21</sup> Furthermore, it is now not enough that  $\delta_1$  and  $\delta_2$  be close together for miscibility to occur. Each of the components of  $\delta_1$  must be similar to the corresponding components of  $\delta_2$ , that is  $(\delta_d)_1 = (\delta_d)_2$ ,  $(\delta_p)_1 = (\delta_p)_2$ , and  $(\delta_h)_1 = (\delta_h)_2$ , for miscibility to occur. Table 25 lists solubility parameters for some solvents. In addition to the three dimensional character of  $\delta$ , temperature, component molecular weight, and molecular weight distribution affect the outcome of a specific blending situation.

The complexities of such a system appear overwhelming and might cause one to lose interest in the solubility parameter approach. This reaction is not entirely justified as discussed in the next paragraph. However, as a result of this

**Table 25. Three Dimensional Solubility Parameters.**

Solvent	Molar Volume (cm <sup>3</sup> /mole)	Solubility Parameter (hildebrands)			
		$\delta^a$	$\delta_d$	$\delta_p$	$\delta_h$
<i>n</i> -Hexane	131.6	7.3	7.3	0	0
<i>n</i> -Octane	163.5	7.6	7.6	0	0
Cyclohexane	108.7	8.2	8.2	0	0.1
Toluene	106.8	8.9	8.8	0.7	1.0
1,1,1-Trichloroethane	100.4	8.6	8.3	2.1	1.0
Methyl ethyl ketone	90.1	9.3	7.8	4.4	2.5
Acetone	74.0	9.8	7.6	5.1	3.4

$$^a \delta = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2}$$

discussion, one will realize that representing the solubility of thermoplastic rubber in solvents as a one-dimensional function of  $\delta$  is incorrect and somewhat misleading for solvents above approximately 9 hildebrands.

**How to Handle Complex Cases.** There is currently no convenient way to handle accurately cases involving polar or hydrogen-bonding components. One-dimensional correlations with  $\delta$  are largely misleading. Two-dimensional correlations involving  $\delta$  and dipole moments or  $\delta$  and hydrogen bonding indexes have been developed<sup>24-26</sup> and may be useful in limited applications. Three-dimensional systems involving computer matching have been developed,<sup>20</sup> but data for real cases are meager. There is considerable interest, especially from the paint industry in developing useful methods for handling solubility parameter, and it is possible that progress in the future may benefit the thermoplastic rubber formulating field.

Meanwhile, it is important that the formulator working with thermoplastic rubber be aware of compatibility concepts as he is preparing and testing formulations. It may be possible to use one, two, or three-dimensional correlations over limited regions, for example, when comparing the relative performance of members of a homologous series in one type of thermoplastic rubber. At the least, solubility parameter may serve as a semi-quantitative basis for planning experiments and for interpreting results.

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# Carboxylic Polymers in Adhesives

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This chapter is based on the chapters which appeared in the two previous editions of this Handbook.<sup>1,2</sup> As stated in the second edition, it is our intent to cover the broad topic of carboxylic copolymers as employed in, or useful for adhesive applications.

Many theories have been proposed in an attempt to explain how carboxylic functional groups improve the adhesion of polymers to various substrates. These groups may act as centers for chemical reactions to effect inter- and intrachain crosslinkages of the polymers as well as linkage to the adherends. It seems probable that acids or other electron accepting groups which enhance adhesion are involved in the transfer of electrons across the interface between the polymer and the adherend. A recent paper on the peel behavior of carboxylated polymers attributes the improved adhesion of a carboxylated polybutyl acrylate copolymer to glass to be caused by two effects: (1) an increase in the thermodynamic work of adhesion and (2) a change in the viscoelastic state of the adhesive material.<sup>31</sup>

## HISTORY

The first carboxylic elastomers were derived by treating rubber and other unsaturated elastomers with maleic anhydride. These anhydride rubbers were then easily converted by moisture

and other hydrolyzing agents into carboxylic elastomers and were first described by Bacon and Farmer<sup>4,5,6</sup> in 1938 and later by Compagnon, Le Bras, and coworkers<sup>7,8,9</sup> in 1941. An anhydride rubber prepared from natural rubber was used as an adhesive agent<sup>10</sup> for bonding rubber to artificial silk in 1944.

A patent<sup>11</sup> issued in 1952 described the use of copolymers of higher acrylate or methacrylate esters with acrylic acid or methacrylic acid in the preparation of improved pressure sensitive tapes and liners for adherent rubber surfaces. The carboxyl content of these copolymers was so high that they could be considered to be plasticized polyacrylic acids rather than carboxylic elastomers.

The preparation of copolymers of butadiene and of isoprene with methacrylic acid and with acrylic acid, described by Frank, Kraus, and Haefner<sup>12,13</sup> in 1952, for use in rubber to metal bonding, was probably the first preparation of carboxylic elastomers made specifically for use as adhesives. They indicated that their consideration of carboxyl groups as a means for enhancing adhesion was stimulated by the observations of Doolittle and Powell<sup>14</sup> in 1944. They found that low proportions of maleic anhydride (0.1–1%) when copolymerized in copolymers of vinyl chloride with vinyl acetate, improved the adhesion of such films to metal surfaces. McLaren has described an increase in adhesion with increasing carboxyl content of vinylite copolymers to unmodified cellulose.<sup>15</sup>

\*Retired

In 1966, a patent<sup>16</sup> was granted to Seibert (B. F. Goodrich) which covered the preparation of carboxyl terminated liquid polymers. These polymers have been used in adhesives and composites as toughening agents, mainly with epoxy resin based systems.

## PREPARATION OF CARBOXYL FUNCTIONAL POLYMERS

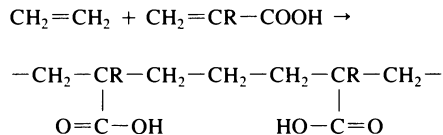
Carboxylic polymers have been prepared principally by the copolymerization of olefins and diolefins with acrylic acid type monomers. References and details concerning such preparations are available in the literature and have been summarized in a review article by Brown.<sup>17</sup> In the preparation of carboxylic elastomers, the types used in adhesives usually contain between 0.1 and 25% of the carboxylic comonomers. Factors influencing the adhesive properties of the carboxylic elastomers are method of polymerization, molecular weight, molecular weight distribution, distribution of the carboxyl groups in the polymer backbone, carboxyl content, the degree of neutralization or sequestering of the carboxyl groups, and the nature of the elastomer backbone.<sup>17</sup>

The adhesive characteristics of an elastomer are recognizably altered by the inclusion of as little as 0.01 equivalent of carboxyl per hundred grams of rubber (ephr) although larger amounts, even in excess of 0.1 ephr, are often preferable. The optimum carboxyl content, molecular weight, and the particular elastomeric polymer selected for use as an adhesive depend on the nature of the surfaces to be adhered and the requirements of the adhesive bond.

Carboxylic elastomers have also been prepared<sup>17</sup> by the addition of a carboxyl-bearing molecule such as thioglycollic acid, maleic anhydride, or acrylic acid to rubber in solvent, on the mill, or in latex. The preparation of a carboxylic polymer from a butadiene-acrylonitrile copolymer in an internal or Banbury mixer has been mentioned in the adhesives patent<sup>18</sup> literature. The carboxylation of vulcanized natural rubber and of butadiene-styrene copolymers, including reclaimed stocks of these elastomers, by treatment with maleic an-

hydride in an extruder plasticator<sup>19</sup> has been described. Elastomeric carboxylic groups have been used<sup>20,21</sup> to prepare carboxylic elastomers. Adducts of fumaric and itaconic esters<sup>22</sup> to unsaturated polymers such as liquid polybutadiene and copolymers of butadiene subsequently hydrolyzed to carboxylic elastomers have also been described as adhesives.

Smarook and Bonotto<sup>23</sup> described the parameters of carboxylic polyolefins made from ethylene and acrylic acid by copolymerization. The ability to vary the carboxyl content on the polyethylene backbone provides resins which have a wide spectrum of physical properties that have exceptional adhesion to various substrates, both polar and nonpolar. The highly polar carboxyl groups in the polymer chain readily enter into covalent, ionic, and hydrogen bonding which can impart various degrees of adhesion and crosslinking with cellulose, metals, rubbers, and plastics. These polymers are produced by the copolymerization of ethylenically unsaturated carboxylic acids with olefins.



Examination of Table 1 indicates that an increase in the acrylic acid content reduces softening point and modulus, which are normally correlated with crystallinity. In addition, tensile strength and adhesion to metallic substrates are increased. Cernia<sup>24</sup> reported similar data on the bulk polymerization of ethylene and acrylic acid which was accomplished at a temperature of  $\sim 200^\circ\text{C}$  and a pressure of 171.6 MPa. The acrylic acid content of the copolymers ranged from 2.1–16%. When used as adhesives for bonding aluminum, the strength of straight polyethylene was 0.003 N/cm as compared to  $>0.59$  N/cm for 16% acrylic acid copolymer.

Rieke and coauthors<sup>25</sup> describe in a series of papers the formulation and properties of grafted polyethylene formed by means of irradiating polyethylene with a Van de Graaff accelerator and then treating the irradiated polyethylene with acrylic acid in a solvent medium. The ad-



**Table 1. Ethylene Acrylic Acid Copolymers.<sup>23</sup>**

	<i>Low Density PE</i>	<i>Increasing AA Content</i>		
Acrylic acid, % wt	—	11	14	19
% moles	—	4.6	6	8.2
Melt index ASTM-D1238-52T, Dg. Min <sup>-1</sup>	1.5	83	58	52
Secant modulus ASTM-D638- 58T, MPa	159	74	60	42
Tensile strength (Instron), <sup>a</sup> MPa	10.3	15.5	19	29
Vicat softening ASTM-D1525- 58T, °C	90	71	63	54
DTA melting point, °C	107	99	98	95
Peel strength to aluminum, N/cm width at cross-head rate of 0.85 mm/s	< 1.75	98	142	175

<sup>a</sup>Rate, 0.85 mm/s, 508  $\mu$ m thick specimen.

hesivity to metals was reported to be markedly improved. In a patent Marans<sup>26</sup> also claims a method of bonding wherein acrylic acid monomer was applied to layers of polyethylene, polypropylene, polyesters, polyvinylchloride, nylon, polymethylmethacrylate, or poly(tetrafluoroethylene) and subsequently irradiated. A review article by Ogata<sup>27</sup> covers the increase in adhesive properties of polyethylene or polypropylene by graft copolymerization of acrylic acid to the polymer in the presence of electron beam radiation.

Carboxyl-terminated liquid polymers (CTLP) can be prepared by using *bis*-cyanoacid initiators and solvents which have low chain transfer to the monomers being polymerized.<sup>16</sup> The initiator starts the polymerization and in the absence of transfer to solvent, terminates the growing chain and yields a carboxyl terminated polymer. Carboxyl groups can also be placed along the chain by using unsaturated acids.

Several other patents<sup>28-32</sup> have been issued covering methods of manufacturing carboxy functional elastomers.

Carboxylic functional polyols can be prepared by reacting hydroxyl terminated polyethers with unsaturated acids and a free radical initiator.<sup>34</sup> Also carboxylic groups can be added to poly(ester/ethers) or other hydroxy terminated polymers by reacting with dianhydrides.<sup>35</sup>

## USE OF CARBOXYLIC ELASTOMERS IN ADHESIVES

The carboxylic elastomers may be employed as adhesives in solution of suitable solvents, as latexes, as aqueous solutions or dispersions in alkaline or ammoniacal media when the carboxyl content and molecular weight are suitably selected. Powders and film products may also be prepared using carboxylic elastomers.

For the preparation of adhesive cements the solubility criteria for the carboxylic elastomers can be predicted from those of analogous non-carboxylic elastomers. Literature<sup>36,37</sup> on the solubility and ease of solution of raw polar elastomers in various solvents, allowing for the influence of the carboxyl level, suggests the solvents most suitable for given carboxylic elastomers. As the carboxyl content increases in a given elastomer type, solubility in hydrocarbon solvents decreases, and solubility in polar solvents increases. Milling procedures are similar to those for analogous noncarboxylic elastomers, except that carboxyl groups tend to make the milling somewhat more difficult. When solid carboxylic elastomers are to be dispersed in solvents, it is best to use methyl ethyl ketone, nitroparaffins, and chlorinated hydrocarbons for the nitrile types. For the carboxylic polyacrylates, acetone, methyl ethyl ketone, methyl isobutyl ketone, and toluene are pre-

ferred. For carboxylic polybutadiene, or copolymers of butadiene, toluene, or methyl ethyl ketone are usually employed.

For some adhesive applications it is advantageous to polymerize the carboxylic copolymers in a solvent medium. Such a procedure avoids emulsifiers and certain other additives of emulsifier polymerization, as well as the necessity of milling. However, it has the disadvantage of yielding lower molecular weight copolymers. While a given carboxylic elastomer may approximate the requirements of many applications and permit a rather wide variety of uses, the maximum performance for a given pair of surfaces to be adhered is best achieved by tailor making the polymer for the selected application. Some degree of adaptation can be achieved by the incorporation of foreign polymers and reagents such as resins, pigments, elastomers, thickening agents, crosslinking agents, and the like.

Powder adhesives can be prepared by reacting carboxylic elastomers with epoxy resins to convert the system into a RT solid which can be ground into a powder. Powders can be electrostatically applied or coated using a fluidized bed. Films are prepared by solvent coating or by melt coating the carboxyl containing elastomer or compound onto a suitable carrier.

### CARBOXYLIC ELASTOMERS AS METAL-TO-RUBBER ADHESIVES

From studies of copolymers of butadiene with methacrylic acid, Frank and coworkers<sup>12,13</sup> concluded that, in order to achieve maximum adhesion of rubber to steel, the copolymer should be of as high a molecular weight as possible and still remain soluble in the solvents of application. It should also possess sufficient diene groups for vulcanization to rubber, and a sufficient number of carboxyl groups to secure high adhesion to steel. They concluded that the optimum level of methacrylic acid was 15–24%. Their data were based on the adhesion to steel of a diphenyl guanidine accelerated natural rubber compound containing 38% zinc oxide and having a 52 Shore A hardness. For their tests, they used a single coat of unmodified, unformulated butadiene-methacrylic acid co-

polymer cement applied to grit-blasted steel inserts and vulcanized 30 min at 150°C against the rubber stock, following ASTM D429-39 procedures. Copolymers of acrylic acid and butadiene or isoprene were less effective as adhesives. Methacrylic acid-isoprene copolymers were less effective than the analogous butadiene copolymers. A butadiene-methacrylic acid copolymer of 70% conversion containing 22–24% methacrylic acid, when used with cumene hydroperoxide accelerators, was reported to give adhesion of rubber to steel having shear strengths of approximately 7.68 MPa.

In the bonding of rubber to metal with unsaturated carboxylic elastomers in the presence of vulcanizing or other agents not reactive with carboxyl groups, the bond to rubber is accomplished by crosslinkages dependent on the unsaturation, while the bond to the metal arises from interaction of polar groups with the metal. This requires fairly simultaneous cures of the cement, the rubber stock and the metal-to-cement interface. When curing agents for the carboxyl groups are also present, the several vulcanizing mechanisms undoubtedly proceed simultaneously and are competitive.

Cements prepared from carboxylic butadiene-acrylonitrile copolymers blended with phenolic resins,<sup>38</sup> like the analogous cements prepared with noncarboxylic butadiene-acrylonitrile copolymers, are adhesive agents for steel to rubber. Employed without curative agents, the carboxylic copolymers give better steel-to-rubber adhesion than the analogous noncarboxylic copolymers. Confirmation of this is cited in the patent literature.<sup>39-41</sup>

Jaeger and Korb<sup>41</sup> described the use of added carboxyl nitrile rubber to modify a standard rubber-to-metal adhesive containing chlorinated rubber and phenolic resin and thereby enhance the rubber-to-metal bonding capability. Cylinders of natural rubber were bonded by vulcanization for 25 min at 145°C and 70 kg/cm<sup>2</sup>. The bond strength for the control adhesive was 59 kg as compared to 74 kg for the modified adhesive. This adhesive was also used successfully for bonding *cis*-polybutadiene rubber and nitrile rubbers to steel, aluminum, and brass adherends. The Dunlop Rubber Company patent<sup>39</sup> claims the use of a butadiene

(37), styrene (36), acrylic acid (18), and methacrylic acid (9) copolymer as a metal primer for rubber-to-metal bonding.

A compounded SBR rubber sheet was surface coated with a copolymer cement derived from butadiene (70), styrene (15), and cinnamic acid (15). The assembly was cured and tested to show peel strength of 210–263 N/cm at a 90° angle. Natural rubber was bonded to aluminum and brass in a similar manner. The carboxylic copolymer cements generally show greater bond strength as well as a desired cohesive failure within the rubber, whereas the analogous noncarboxylic copolymers show failure at the steel surface. Thus carboxyl groups enhance the adhesion of the rubber to the metal surface and improve the cohesive strength of the bonding agent. Inclusion of carboxyl groups in the butadiene-acrylonitrile copolymers widens their range of compatibility with phenolic resins and increases the strength and hardness of the resultant adhesive.

### CARBOXYLIC ELASTOMERS IN ADHESIVES FOR NONMETALLIC ADHERENDS

Dispersions of copolymers of butadiene with acrylic acid or methacrylic acid in aqueous potassium hydroxide have been mentioned in the patent literature<sup>42</sup> as a dip for adhering *rayon tire cord to rubber*. The effect is most evident when carboxyl groups are present in the adhesive, the tie cement, and the cover stocks. The adhesive may be applied as latex, aqueous dispersion, or cement. A patent issued to the Dunlop Company Ltd.<sup>43</sup> describes the use of a styrene-butadiene-itaconic acid copolymer with Gen-Tac Latex (GenCorp) in formulating an RFL (resorcinol formaldehyde latex) type adhesive for bonding a natural rubber compound to Nylon 66 and rayon tire cords. Brodnyan<sup>44</sup> also claims carboxylic adhesives for rayon, nylon, and Dacron cords. In this case, the tire cords were treated with a mixed polymer latex containing resorcinol-formaldehyde condensate, a butadiene-vinyl pyridine copolymer, an SBR copolymer, and a multifunctional copolymer from methyl acrylate, 2-hydroxypropyl methacrylate, and acrylic acid. A different approach was reported by Badenkov<sup>45</sup> whereby rayon or nylon tire cords were coated with

binder compounds during the spinning operation. SKD-5 (19:1 butadiene-methacrylic acid) copolymer was combined with FR-12 (resorcinol-formaldehyde resin) to form the binder coatings. In related work on tire carcass cord bonding, Dostyan and coauthors<sup>46</sup> showed a computer assisted statistical analysis of the optimum amounts of modifier RU-1, methacrylic acid, and FR-12 (resorcinol-formaldehyde resin) in carboxylic latex SKD-1 and latex DSVP-15 containing vinyl pyridine functional groups.

The bonding of fibers of paper, fabric or similar materials by rubber latexes or cement may be enhanced by the inclusion of carboxyl groups<sup>47</sup> in the adhesive or binder copolymer molecules. For example, in the bonding of semi-bleached kraft crepe paper with polyethyl acrylate latex, the inclusion of 0.045 ephr of carboxyl gave approximately a 50% further improvement in internal bond strength. Similarly, while a butadiene-acrylonitrile copolymer improved the internal bond strength of semi-bleached kraft crepe paper, a latex of a copolymer having the same butadiene content but including 0.09 ephr of carboxyl, showed a 15% or more additional improvement in the internal bond strength. The beneficial action of the carboxyl group is probably due to improvement in copolymer adhesive penetration and subsequently greater hydrogen bonding with the paper cellulose.

In cotton-cotton lamination, the use of carboxylic elastomer latexes is reported<sup>48</sup> to double the bond strength and improve the solvent resistance over that normally found with conventional noncarboxyl latexes. A typical copolymer latex was based on isoprene (54–64), acrylonitrile (35–45), and methacrylic acid (1–3). A Dow Chemical Company patent<sup>49</sup> claims the use of a film-forming carboxylic copolymer latex, an epichlorohydrin-polyamide adduct, with a calcium carbonate filler as an improved adhesive for bonding scrim to the back of tufted carpeting.

### CARBOXYLIC ELASTOMERS AS METAL-TO-METAL ADHESIVES

Carboxylic butadiene-acrylonitrile copolymers have been employed in blends with selected phenolic resins as metal-to-metal adhesives.<sup>50</sup>

Hycar 1072 CG rubber gives bonds similar to the noncarboxylic polymers in both curing and noncuring systems. In combination with epoxy resins, Hycar 1072 imparts elongation, elasticity, and resilience and has been used extensively in bonding rigid adherends including metals. Clougherty<sup>51</sup> claims thermally stable, high strength adhesives for bonding rigid brake linings to metal shoes by modifying a thermosetting phenolic resin with Hycar 1571 latex, a carboxyl-containing butadiene-acrylonitrile polymer. The use of maleic anhydride elastomer adducts in adhesives for metals has been mentioned<sup>19,52</sup> in the literature.

The inclusion of carboxyl groups in polyethyl acrylate improves the adhesion to steel.<sup>53</sup> This is shown graphically in Fig. 1, where increasing the carboxyl content from zero to about 0.2 ephr provides a corresponding increase in steel-steel lap shear strength from 0.69 to 6.9 MPa. These values were obtained with uncompounded copolymers. Larger amounts of carboxyl and reinforcing resins can be used to achieve even higher bond strengths.

Terpolymers of ethyl acrylate, acrylonitrile, and acrylic acid have been cited as thermosetting adhesives for aluminum.<sup>54</sup>

A poly(ester/ether) blocked copolymer<sup>35</sup> was reacted with a dianhydride to yield a carboxylated thermoplastic having very high peel and tensile strength when bonding to metal substrates. Furthermore these carboxylated thermoplastics were crosslinked with a diepoxide to yield an adhesive for metal which had higher temperature creep resistance.

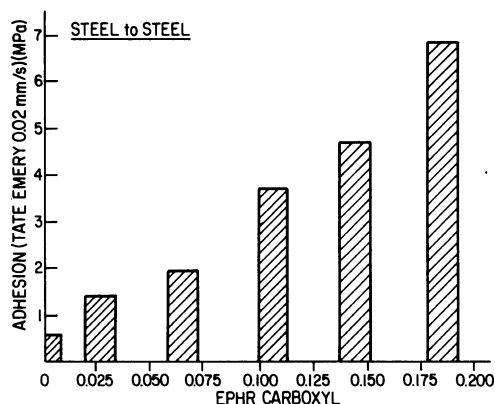


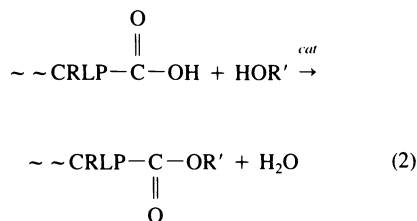
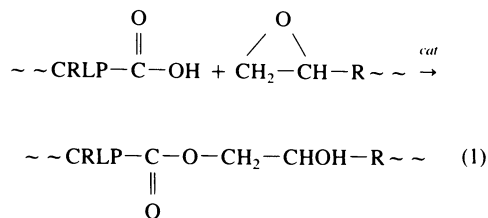
Fig. 1. Adhesion as a function of carboxyl content in carboxylic polyethyl acrylates.

## CARBOXYL REACTIVE LIQUID ELASTOMERS IN STRUCTURAL ADHESIVES AND COMPOSITES

During the past several years there has been extensive use of carboxyl functional liquid nitrile copolymers for toughening structural plastics, adhesives, and composites such as those made from crosslinked epoxy resins. The term *toughening* is used to denote a marked increase in impact resistance and an ability to absorb energy without catastrophic fracture. This phenomenon of toughening occurs without appreciable loss of mechanical properties such as is normally seen with flexibilized crosslinked resins. As applied to structural adhesives, it is observed that the area under the stress-strain curve is tremendously increased without significant loss of tensile strength or heat resistance. This feature has made this technology of great interest to the adhesives industry.

Carboxyl reactive liquid polymers (CRLP)<sup>55</sup> are chemically reactive with epoxy resins and capable of chain extension and crosslinking through the carboxyl groups. The reactions most important in adhesive applications are those with epoxide groups and with aliphatic hydroxyl groups. A list of several commercially available CRLP products is shown in Table 2.

A weak amine catalyst will cause reaction (1) to be predominant.<sup>56</sup> If a strong acid, i.e., *p*-toluenesulfonic acid, is used, reaction (2) will be predominant. Therefore CRLP with termi-



**Table 2. Properties of Carboxyl Reactive Polymers.**<sup>55</sup>

	<i>Hycar</i> <i>CTB</i> (2000 × 162)	<i>Hycar</i> <i>CTBN</i> (1300 × 15)	<i>Hycar</i> <i>CTBN</i> (1300 × 8)	<i>Hycar</i> <i>CTBN</i> (1300 × 13)	<i>Hycar</i> <i>CTBNX</i> (130 × 9)
Brookfield viscosity at 27°C, MPa·s	35,000	50,000	125,000	625,000	135,000
Percent acrylonitrile	—	10	18	28	18
Color	light	amber	amber	amber	amber
Molecular weight, $M_n$	4,000	3,600	3,400	3,400	3,400
Carboxyl functionality	2.01	1.90	1.85	1.80	2.4
EPHR carboxyl	0.045	0.051	0.055	0.055	0.077
Specific gravity at 25/ 25°C	0.097	—	0.948	—	0.955
Heat loss, 2 hr at 130°C, %	0.5	1.0	1.0	1.0	1.0
$T_g$ (by DTA), °C	-80	—	-59	—	-54

nal reactivity, when added to a difunctional epoxy resin and a weak selective<sup>56,57</sup> catalyst, results in chain extension through epoxy carboxylic reactions. It is necessary to carefully control this reaction to yield a prereact that is reproducible and suitable for a particular adhesive formulation. If reaction conditions are not controlled, side reactions can result in higher epoxide equivalent weights and partial crosslinking. This of course can yield different properties in the final adhesive. It is important that a particular system be studied to determine the correct CRLP and suitable reaction conditions.

Crosslinking can then be accomplished by using a polyfunctional acid or epoxy resin or through the use of curatives such as aromatic and aliphatic amines, dicyandiamide, or Lewis acids. Curing can take place at ambient temperature to 177°C but the most highly toughened adhesives are generally cured at 120°C.

There are now commercially available pre-reactions of CRLP and liquid epoxy resins<sup>58,59</sup> which can be used to toughen adhesives.

The early work of McGarry and coworkers<sup>60</sup> revealed that brittle epoxy resins could be toughened by incorporating small amounts of CRLP. The most effective polymers are copolymers of acrylonitrile and butadiene (Hycar CTBN). The level of acrylonitrile can be varied from 0 to 28%. Also additional acid groups can be inserted into the polymer chain. Analysis of fractured surfaces reveal a two-phase system

with small rubber particles embedded in the glassy epoxy matrix. These types of materials appear to be toughened only at temperatures near 25°C. In adhesive applications and especially structural adhesives any improvement in toughness must be effective over the entire range of temperatures encountered in service. Proprietary work by adhesive manufacturers has been concerned with toughening epoxy resins for use in structural adhesives.<sup>61,62,63</sup> Several products have been toughened with Hycar 1300 × 8, 1300 × 9, 1300 × 13 and 2000 × 162. Several products also utilize a high molecular weight carboxylated acrylonitrile-butadiene copolymer, i.e., Hycar 1072.<sup>61</sup> This combination of high molecular weight and low molecular weight carboxyl functional polymers yields a bimodal distribution of rubbery particles which appears to be necessary for developing good properties across a broad temperature range.

Several sources have shown that toughness can be improved if a dihydric phenolic, i.e., bisphenol A, is added to the epoxy resin and CRLP.<sup>64</sup> It is reported that this formulation yields a bimodal distribution of particles when cured with piperidine and utilizing 5 phr of Hycar CTBN (1300 × 8). This bimodal distribution of rubber particles gives adhesives with higher fracture toughness and good peel properties over a broad range of temperatures. Two patents<sup>65</sup> have been issued covering work using 1,5-naphthalenediol, bisphenol A, resorcinol

**Table 3. Formulation and Properties of Structural Adhesive Films Using Dihydric Phenolics.**

	<i>A</i>	<i>B</i>	<i>C</i>
Epoxy resin (i.e., Epon 828)	98	48	103.5
1,5-Naphthalenediol	12.4	—	—
Bisphenol A	—	18	—
2,2-bis(4-hydroxyphenyl)sulfone	—	—	18
Hycar CTBNX	15	15	15
A-C reacted 1 hr at 130–160°C, then add dicyandiamide	8	8	8
2-ethyl-4-methylimidazole	1	1	1
121°C lap shear (MPa)	22.4	10	22.1
T-Peel at 25°C (N/cm)	42	44	—

Cured 1 hr at 121°C.

and 2,2-bis(4-hydroxyphenyl)sulfone along with Hycar 1300  $\times$  9 to produce tough epoxy resin based structural adhesive films (Table 3).

Although most of the development work in toughening of epoxy resins has made use of some type of prereaction with carboxylic nitrile copolymer in the presence of a suitable catalyst, various techniques have been used to accomplish this. Generally the epoxy resin and the CRLP are reacted with heat and agitation to give whatever combination of reaction products that are desired. This depends upon the type of epoxy resin, the type of CRLP, the catalysts and the reaction conditions.

Clark<sup>66</sup> introduced a copolymer into epoxy resin in the form of a latex which was vacuum stripped and reacted. However, the surfactants are not easily removed and can cause the resultant product to be moisture sensitive.

The variation of the ratio of epoxy resin to CRLP can give cured systems resembling either rubber toughened plastics or epoxy reinforced rubbers. By varying the epoxy resin to CRLP ratio and by varying the type of CRLP and epoxy resin one can prepare compositions which could bond a variety of substrates providing the proper curing agents and curing conditions are used.

CRLP's have also been used to toughen epoxy resins used in composite applications. This has not been as fruitful an area as toughening of adhesives for a variety of reasons too complex to be discussed here. However, excellent publications covering composites and composite properties are available.<sup>67,68</sup>

### PARTICULATE STRUCTURAL ADHESIVES USING CARBOXYLATED RUBBERS

Reaction products of solid epoxy resins, e.g., DER 664 (Dow), and Hycar carboxyl reactive liquid polymers can be used to toughen solid epoxy resins for use in powder adhesives or coatings<sup>69</sup> (see Table 4).

Particulate structural adhesives have also been prepared by the combination of epoxy resins and elastomeric carboxylated rubber, Hycar 1072. The epoxy resins are milled into the rubber and then the curatives are added. The stock is sheeted from the mill and ground into a powder. The adhesives can be applied by electrostatic spraying, fluidized bed, or powder bed.<sup>66,70</sup>

**Table 4. Typical Formulation for Particulate Structural Adhesive.<sup>68</sup>**

	<i>Parts</i>
Epoxy Resins	
Epon 1002 (Shell)	89
ECN 1280 (Ciba) (epoxidized cresol novolac resin)	11
Hycar 1300 $\times$ 8	36
Dicyandiamide	3.5
Monuron (DuPont (3- <i>p</i> -chlorophenyl-1,1-dimethyl urea)	2.25
T-Peel at 24°C, N/cm	42
82°C lap shear, MPa	14.7
121°C lap shear, MPa	5.2

Cured 1 hr at 120°C.

## CARBOXYLIC ELASTOMERS AS PRESSURE-SENSITIVE ADHESIVES

The carboxylic polyacrylates are effective as laminating adhesives<sup>52</sup> for both flexible and rigid surfaces. The particular carboxylic acrylate used for a given laminating application is determined by the characteristics of the surfaces to be adhered, whether adhesive or cohesive bond failure is desired, the bond strength required of the adhesive, and many other factors. These may include stiffness, friability, extensibility, clarity, cold flow, moisture resistance, solvent or chemical resistance, heat and light insensitivity, radiation resistance, compatibility with resins and other polymeric materials or pigments, and vulcanizability. The carboxylic polyacrylates may be varied to meet the adhesive requirements of a specific application by:

1. Carboxylic content,
2. The acrylate or acrylates constituting the polymer chain,
3. Molecular weight,
4. Molecular weight distribution,
5. State of crosslinkage,
6. Degree of inter- and intrachain reactivity induced by the inclusion of other functional groups in addition to carboxyl,
7. Degree of solubility or dispersibility in solvents of application, and
8. Copolymerization or superimposed polymerization.

The influence of carboxylic groups on the laminating power of permanently tacky adhesive copolymers used in non-load-bearing applications is well illustrated by the performance of polyacrylates<sup>53</sup> in the lamination of Mylar (duPont polyester) films to aluminum foils, each 1 mil thick. Noncarboxylic polyacrylate polymers are weak laminating adhesives for Mylar to aluminum bonding. The adhesion varies with the polyacrylate used. In a series of comparable poly-*n*-alkyl acrylates, ranging from polymethyl through polytridecyl acrylate, applied from methyl ethyl ketone cements, the strongest bond (180° peel strength) between Mylar and aluminum was obtained with polyethyl acrylate. A value of 8.8 N/cm for a separation rate of 5.1 mm/s was typical for noncarboxylic polyethyl acrylate (Fig. 2). The peel

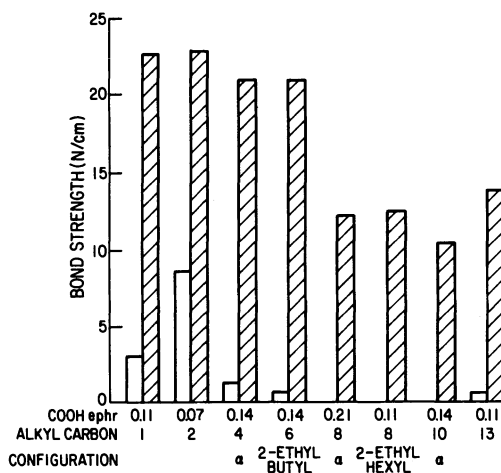


Fig. 2. Influence of carboxyl content on Mylar-to-aluminum bond strength of polyacrylate adhesives.

strength enhancement using the corresponding carboxyl acrylates is most striking. The carboxyl contents of the copolymers are expressed as equivalents per 100 grams of rubber (ephr).

The patent literature on carboxylic polyacrylate pressure-sensitive adhesives is extensive. Korpman<sup>71</sup> describes the use of carboxylic butadiene-acrylonitrile copolymer (Hycar 1072) in conjunction with tackifying resins and a butylated melamine-formaldehyde curing resin as a pressure-sensitive adhesive on a polyester film backing. The composite sheet was useful as a pressure-sensitive adhesive after air drying and curing for 1 min at 120°C, whereas, noncarboxylic elastomers remained uncured after 1 hr at 120°C. A copolymer of 2-ethylhexyl acrylate, methyl acrylate, glycidyl methacrylate, and acrylic acid was reported by Knapp<sup>72</sup> to be so pressure-sensitive that it would bond polyester film to a steel sheet and resist a shear loading of 1.8 N/cm<sup>2</sup> at 60°C without creeping. One of the useful attributes of pressure-sensitive adhesive tapes made with carboxylic polyacrylates is that essentially no compounding is required provided that proper balance of creep, peel, shear, and tack properties are built into the elastomer during its preparation.<sup>53,73</sup> Another interesting way of altering the tack, peel strength, and creep resistance of carboxyl functional pressure-sensitive adhesives is through partial ionic bonding of carboxyl groups with metal ions.<sup>74</sup> In general, modulus increases, tack and peel strength decrease, but

resistance to creep increases in relation to the degree of ionic bonding. Such modified polymers exhibit some characteristics typical of crosslinking. A significant difference is that ionic bonding, while effective at room temperature, is greatly weakened at elevated temperatures. This property permits easy processing by the simple expedient of raising the operating temperature.

Some pressure-sensitive tapes including surgical tapes have been reported to contain carboxylic acrylate copolymers.<sup>75,76,77</sup> A pressure sensitive tape consisting of foil, polyester, polyolefin, or acrylic adhesive layer and a carboxylated polymer-aminofunctional silane primer layer has been patented.<sup>78</sup> The silane alone is reported to interfere with adhesion of the tape to the substrate; but excellent adhesion is obtained if a carboxylated EVA copolymer is added to the primer.

#### **ADHESION WITH NONELASTOMERIC, CARBOXYL FUNCTIONAL, OLEFIN COPOLYMERS**

It was reported by Doolittle and Powell<sup>14</sup> as long ago as 1944 that the adhesive qualities of vinyl polymers were enhanced through the addition of maleic anhydride. Since then much information has appeared on the adhesive nature of carboxylated olefin copolymers. Guthrie<sup>79</sup> was issued a patent in 1971 which claims that polar copolymers of olefins containing pendant carboxylic acid groups may be bonded to wood, metals, and other substrates. Sato and coauthors<sup>80</sup> found enhanced adhesive qualities by using a grafted copolymer product obtained by reacting an ethylene-vinyl acetate copolymer with a carboxylic acid, and in 1973, Steinkamp and coauthors<sup>81</sup> reported that modified polyolefins with <5% acid functionality showed improved bonding to reinforcing inorganic fibers such as asbestos, glass, and aluminum. They also described a series of acidic olefin copolymers which bond tenaciously to unprimed metals such as copper, lead, steel, and aluminum as well as glass and some thermoplastics. Their physical, chemical, and adhesive properties suggest use in wire and cable coverings.

Waxy adhesive products have been prepared

by grafting small amounts of maleic anhydride on polyolefins. Incorporation of the polar monomer improved adhesion to polar textiles, metals, and plastic films. Thermal grafting of maleic anhydride or maleic acid to polypropylene gives waxy adhesives useful for aluminum-paper laminates.<sup>63</sup> Although itaconic acid is considerably more expensive than the other major carboxylic monomers, it has gained acceptance as a comonomer in specialty applications. It is a more active monomer than maleic or fumaric acids and can therefore be incorporated into copolymers more readily. Copolymers of vinylidene chloride, acrylic comonomers, and itaconic acid have considerable commercial utility in packaging. The incorporation of the acid provides strongly bonded heat seals that are resistant to boiling water. When a 95:5:2 latex copolymer of vinylidene chloride, methyl acrylate, and itaconic acid was applied to cellophane film the heat seal strength was 2.36 MPa as compared to 0.91 MPa for a copolymer lacking the acid.<sup>84</sup>

#### **CARBOXYLIC POLYMERS IN HOT-MELT ADHESIVES**

Several publications have described the basic properties of carboxylic polyethylene copolymers including their adhesive characteristics.<sup>85,86,87</sup> In general, increasing acrylic acid content results in increasing both tensile strength and flexibility which are important both for adhesion and bond retention under aggressive environmental attack.<sup>23</sup> In flexible hot-melt packaging applications, the use of ethylene-acrylic acid (EAA) copolymers provides improved hot tack and reduced heat seal temperatures. EAA copolymers achieve the contact angle characteristics of hot melts and also exhibit superior cohesive strength. Increasing the carboxyl content does have some effect upon water sensitivity. However, water absorption is relatively low even at a 20% AA content (0.08% wt increase after one week at RT).<sup>23</sup> Tensile strength and elongation are not significantly changed. It has been observed that the bond strength shows a greater decrease after moisture exposure when bonding to metal adherends rather than to nonpolar types such as low density polyethylene. In general, the best



polymer for adhesion of composite structures may be obtained by balancing polymer performance in relation to water sensitivity and the substrate to be used. Metal substrates are best bonded with the medium range (15% AA) carboxyl polymers while nonpolar materials should be bonded with low AA (3%) polymers.

Hot-melt adhesives for packaging applications have been formulated using carboxyl polymers in combination with many other materials. A discussion of the properties of ethylene-ethyl acrylate (EEA) copolymers as raw materials for heat sealing and thermoplastic adhesives was presented by Kirckner in 1969.<sup>88</sup> The patent literature is replete with claims concerning the formulation, use, and properties of hot-melt adhesives containing a variety of carboxyl copolymers.<sup>89-92</sup> Guiman<sup>93</sup> reported that thermoadhesive films have been made by the radiochemical grafting of high density polyethylene with acrylic acid. Two additional patents<sup>94,95</sup> described the coextrusion of nylon, carboxyl olefin, and polyethylene to produce a self-supporting multilayer film having a nominal thickness of only 1 mil. These laminates which are useful in packaging, have high strength, toughness, and clarity, excellent sealability, and firm bonding between the layers.

The development of high strength thermoplastic adhesive copolymers of the EEA type containing reactive carboxyl groups has made it practical to bond insulation such as polyethylene to metal conductors to provide adequate bonding and long term environmental resistance. Frequently, the EEA copolymer is extruded around the cable. Peacock<sup>90</sup> reports that when a layer of acrylic acid-ethylene copolymer (7:43) was extruded at 140°C over a flexible aluminum conductor followed by a layer of polyethylene insulation, the bond strength between the insulation and the conductor was 72 N/cm compared with 1.4 N/cm for a control assembly without the copolymer adhesive. There are numerous similar patent claims for insulated conductor cable.<sup>97,100</sup>

### **CARBOXYL FUNCTIONAL VINYL COPOLYMER RESINS IN ADHESIVE APPLICATIONS**

The incorporation of small amounts of maleic anhydride or maleic acid into copolymers of vi-

nyl chloride and vinyl acetate substantially improves their adhesion. The typical range of compositions of commercial products, such as Vinylite VMCH is 85-88 : 11: 1-3 vinyl chloride-vinyl acetate-maleic anhydride. Applications for these terpolymers include heat sealing of packaging films and vinyl plastisols with improved adhesion to substrates.<sup>101-103</sup>

Vinyl dispersion resins have typically consisted of inert homopolymer or copolymers of vinyl chloride and vinyl acetate, and although the inertness has been of importance for a multitude of applications, there are occasions when reactive functionality is an aid. An example of such a reactive vinyl resin is Geon 137, a carboxyl modified dispersion resin with a carboxyl content equivalent to 1.79% on a resin weight basis or an acid equivalent weight of about 2500.<sup>104</sup> One adhesive application of considerable interest is in the production of flocked product, notably wall and floor coverings. A 50% replacement of standard copolymer dispersion resin with carboxyl functional resin doubles the force required to pluck fibers loose. Test results of laminating carboxylic vinyl plastisol with nylon fabric have shown a three-fold increase in adhesion.<sup>104</sup> Such plastisols also show improved adhesion to glass and polyester fabrics.<sup>105</sup>

Strong durable bonds can be formed between metals and vinyl chloride polymers by using a polymeric adhesive which contains carboxyl groups and a phenol formaldehyde resin.<sup>106</sup>

Plasticized PVC and vinyl chloride-vinyl acetate copolymers can be wiped with solutions of adipic, maleic, citric, and other acids, giving improved adhesion when bonding with hot-melt polyester adhesives.<sup>28</sup>

### **CARBOXYLIC FUNCTIONAL NEOPRENES AS CONTACT ADHESIVES**

Smith<sup>77</sup> has described in detail the practical advantages of carboxyl functional Neoprenes AF and AJ for making improved contact adhesives. The early room temperature bond strength of conventional neoprene contact adhesive is dependent on the crystallization rate of the polymer. Single component adhesive systems based on carboxyl functionality undergo crosslinking reactions with divalent

metal oxides such as magnesium oxide. The crosslinks formed in this manner have the reversible character typical of ionic bonds, and the reversibility is used to inhibit gelation in solution. The early hot bond strength of a Neoprene AF based adhesive is considerably higher than that of an adhesive based on the noncarboxylic Neoprene AC when rubbers have a comparable Mooney viscosity.<sup>77</sup> The effect of the carboxyl groups in Neoprene AF is also quite pronounced at room temperature. Bond strength development is rapid in an AF adhesive as compared to an AC adhesive even when the bond is assembled wet.

Carboxylated Neoprene latices<sup>107</sup> have been reported to have good contact adhesive properties without the problem generally related to the use of solvents.

## MISCELLANEOUS USES OF CARBOXYLATED ELASTOMERS

Several patents<sup>108-112</sup> have been issued covering various uses of carboxylic functional elastomers and the resultant improvement in adhesion of a variety of substrates when carboxyl groups are added to the polymer chain.

A patent issued in 1976<sup>113</sup> also shows that polyfunctional carboxylic aziridinylester can be incorporated into vinyl resins to give improved adhesion to metals and glass without using primers and other adhesion promoters.

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# Neoprene (Polychloroprene)-Based Solvent and Latex Adhesives

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Neoprene, or *polychloroprene*, was the first synthetic elastomer used by the adhesives industry, and is one of the most versatile materials ever developed as a backbone for elastomeric adhesives. Neoprene combines rapid bond strength development with good tack or auto-adhesion, and resistance to degradation by oils, chemicals, water, heat, sunlight, and ozone. It is popular in numerous areas such as shoe sole attachment, furniture construction, automobile assembly, and a variety of construction applications.

The domestic consumption of Neoprene in adhesive applications will be approximately 30 million dry pounds in 1990. From one-quarter to one-third of this amount will be in latex form.

## HISTORY

Neoprene was the first synthetic elastomer developed which had many of the properties of natural rubber. Its development began when Dr. Nieuwland of Notre Dame synthesized divinyl acetylene from acetylene using  $\text{CuCl}$  as a catalyst. DuPont scientists, learning of his research, joined Dr. Nieuwland in pursuing the possibility of producing a synthetic elastomer from acetylene chemistry. In the late 1920s, they found that by varying the reaction condi-

tions, monovinylacetylene could be readily prepared, with divinylacetylene present only as an impurity. They also discovered that monovinylacetylene could be reacted with hydrochloric acid to form *chloroprene*, 2-chloro-1,3-butadiene, which formed a rubberlike polymer upon polymerization.

The first public announcement of this polymer was made in 1931; commercialization began in April 1932. At first known as "DuPrene," the polymer was designated "Neoprene" by DuPont in 1936.

Prior to the second World War, natural rubber was the only elastomer widely used in adhesives. It was used for such applications as tire building, adhering of sponge weatherstrips to automobile doors, and the temporary attachment of shoe soles. However, rubber cements were limited by their low cohesive strength and poor aging of the uncured film.

Following its development in 1931, DuPont Neoprene was slow in displacing natural rubber in the adhesive industry for the following reasons:

1. It was high in price, selling for two or three times the price of natural rubber.
2. It had to be dissolved in aromatic solvents, which were several times as costly as the petroleum naphtha used to dissolve natural rubber.

3. It was necessary to use about five times as much Neoprene as natural rubber to obtain equivalent viscosities.

The situation did not change until 1942, soon after the start of World War II. At that time, a critical shortage of natural rubber developed because it was allocated chiefly for the war effort. Neoprene was chosen as a replacement for natural rubber in adhesives because it was the only other synthetic rubber available. Animal glue and other water-soluble materials available at the time were unsatisfactory because of their slow drying rates, poor adhesion to many surfaces, inflexible films, and rusting of metals. The two Neoprene polymers available at the time were Neoprene GN, a general purpose type, and Neoprene CG, a fast-crystallizing type. Both are copolymers of chloroprene and sulfur which contain a thiuram disulfide modifier.

One of the first applications in which Neoprene proved satisfactory was in the shoe industry, for both temporary and permanent sole attachment. However, early Neoprene cements were plagued by two problems: a decrease in viscosity on aging and a black discoloration during storage in steel drums.

The discoloration was found to be caused by trace amounts of hydrochloric acid which form when Neoprene oxidizes on aging. This acid reacts with iron to form ferric chloride, which in turn reacts with the thiuram disulfide modifier to form a black iron sulfide compound. Acid acceptors such as magnesia and zinc oxide were found to be effective in preventing this discoloration. However, their addition tended to decrease the viscosity stability of adhesive cements even further.

The stability of Neoprene cements containing metal oxides could be increased with about 10 parts of hydrated calcium silicate, (e.g., Silene EF, PPG Industries) or terpene phenolic resin (e.g., Durez 12603, Occidental Chemical Co.). The presence of the former increased the cohesive strength of Neoprene about threefold, while the latter lowered its cohesive strength at elevated temperatures.

Neoprene type AC, developed in 1947, has somewhat better viscosity stability and resistance to discoloration than the sulfur-modified

G types, but cures considerably more slowly at room temperature.

Neoprene type AD, developed in 1958, is considerably more stable than AC. It does not change color appreciably when in contact with iron, and solutions maintain stable viscosities over longer time periods. Neoprene AC and AD are now considered the general purpose types for solvent-based adhesives. They will be discussed in more detail, along with other Neoprene solvent types and latexes commonly used in adhesives, in the following sections.

Neoprene was manufactured via the acetylene route for many years. However, the technology is difficult and the starting material, acetylene, gradually increased in price over the years. By 1960 a second, less expensive method of chloroprene production had been developed and commercialized. The second, preferred method involves the production of chloroprene from *butadiene* via a *chlorination* step.

## THE EFFECT OF POLYMER STRUCTURE

Neoprene is produced from the chloroprene monomer, 2-chloro-1,3-butadiene, in an emulsion process. During polymerization, the monomer can add in a number of ways as shown in Table 1. The proportion of each configuration determines the amount of *crystallinity* in the polymer and its reactivity.

The *trans*-1,4 addition is the most common. Very high percentages of this structure give high crystallinity and rapid bond strength development in contact adhesives. Neoprene AC and AD, both fast crystallizing grades, contain about 90% *trans*-1,4 structures; whereas Neoprene W, a slow-crystallizing type, contains only 85% *trans*-1,4. The other three types of monomer addition shown decrease bond strength development and lengthen open time by disrupting polymer crystallinity. In addition, the 1,2 structure provides active sites for polymer vulcanization.

The ability of Neoprene adhesives to crystallize sets them apart from other elastomeric binders. As a result of crystallization, their cohesive film strength is much greater than that of amorphous polymers. Crystallization is a reversible phenomenon, and at temperatures over

**Table 1. Molecular Structure of Neoprene.**

Chloroprene Monomer	
	$\begin{array}{c} \text{Cl} \\   \\ \text{CH}_2 = \text{C} - \text{CH} = \text{CH}_2 \end{array}$
Type of Addition	Formula
trans-1,4	$\begin{array}{c} \sim\text{CH}_2 - \text{C} = \text{C} - \text{H} \\   \quad \quad   \\ \text{Cl} \quad \quad \text{CH}_2 \end{array}$
cis-1,4	$\begin{array}{c} \sim\text{CH}_2 - \text{C} = \text{C} - \text{CH}_2 \\   \quad \quad   \\ \text{Cl} \quad \quad \text{H} \end{array}$
1,2	$\begin{array}{c} \sim\text{CH}_2 - \text{C} \sim \\   \\ \text{CH} \\    \\ \text{CH}_2 \\   \\ \text{Cl} \end{array}$
3,4	$\begin{array}{c} \sim\text{CH} - \text{CH}_2 \sim \\   \\ \text{C} - \text{Cl} \\    \\ \text{CH}_2 \end{array}$

52°C (126°F) uncured adhesives lose their high cohesive strength. Upon cooling, the film recrystallizes and cohesive strength is regained. A comparison of Neoprene AD, a fast-crystallizing type, and Neoprene AF, a reactive polymer, with several other elastomers is shown in Fig. 1. In addition to high film strength, crystallization is responsible for the *quick grab* for which Neoprene adhesives are noted. This rapid bond strength development allows the formation of immediate dry bonds without the need for further clamping, pressing, or airing. Since Neoprene polymers are produced which crystallize at various rates, the adhesive compounder can use polymer blends to get the balance of properties he requires. The effect of crystallinity on polymer properties is summarized in Fig. 2.

The Neoprene polymers also vary in the amount of branching present in the polymer. Those which have little or no branching are re-

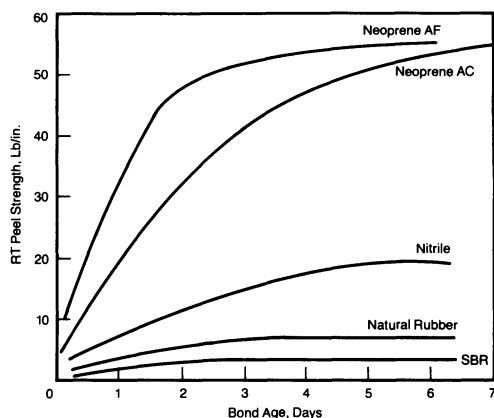


Fig. 1. Canvas/canvas bond strength development: neoprene vs. other elastomers.

ferred to as *sol polymers*, while those with considerable branching are referred to as *gel polymers*. All of the solvent grade polymers, with the exception of Neoprene AG, are sol polymers. They are highly linear and soluble in aromatic solvents. The Neoprene latexes, on the other hand, vary widely in the percentage of polymer gel. As shown in Fig. 3, properties which are affected by the amount of gel in the polymer include cohesive strength, resilience, resistance to permanent set, elongation, open tack time and oil swell. Thus, particularly in latex systems, varying the gel content of the system through polymer choice offers another means of adjusting adhesive properties.

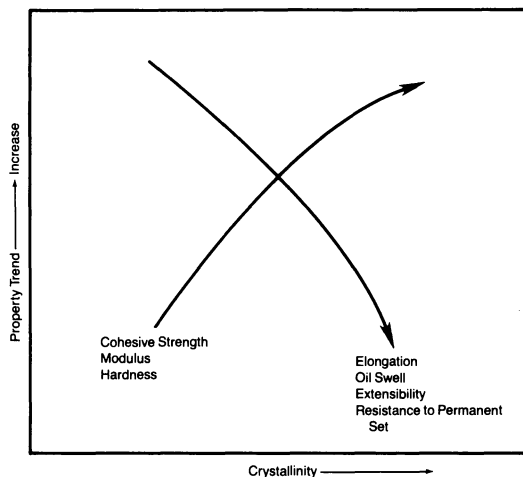


Fig. 2. Effect of crystallinity on polymer properties.

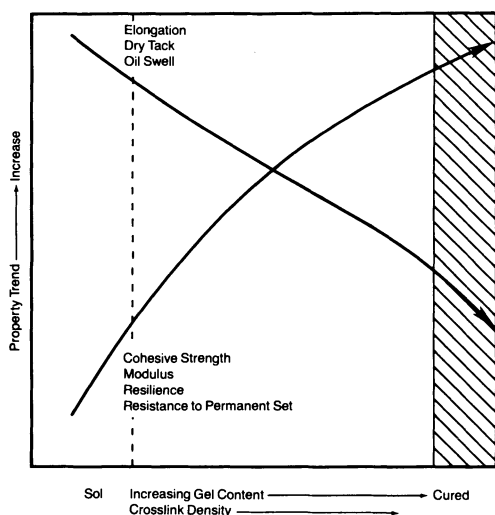


Fig. 3. Effect of sol, gel, and curing on polymer properties.

### NEOPRENE SOLVENT-BASED ADHESIVE CEMENTS

Neoprene provides a versatile elastomeric base in the formulation of solvent based adhesives. Properly compounded adhesives are resistant to degradation from exposure to heat, sunlight, ozone, water, oils, and chemicals. Neoprene can be dissolved in many solvent blends to give adhesive solutions which are stable for extended periods of time. Solvent selection, therefore, allows a great deal of variation in adhesive viscosity and drying rate. Other com-

pounding ingredients, particularly resins, are used to achieve good specific adhesion to many porous and nonporous substrates. The compounding versatility associated with Neoprene adhesives allows the formulation of one-part contact cements, two-part curable adhesives, pressure-sensitive adhesives, and mastics and caulks.

### Types of Neoprene

The principal types of Neoprene used in solvent adhesives are summarized in Table 3, along with their physical properties. Neoprene AC and AD are considered the general purpose adhesive types. Because they crystallize rapidly, both give quick grab and high uncured strength. When properly formulated, they also give good application properties and resistance to heat and phasing. Most adhesive manufacturers prefer Neoprene AD over Neoprene AC because it offers superior viscosity stability in both raw polymer and adhesive form.

The fast crystallizing types are widely used in shoe sole attachment, adhering decorative high pressure laminates and automotive trim and in many other industrial applications. A general purpose adhesive formulation is presented in Table 2.

Neoprene AD-G is a Neoprene AD variant designed especially for use in grafting applications, although it is suitable for use in standard contact bond formulations as well. In the

Table 2. Neoprene Contact Bond Adhesive.

<i>General Formulation</i>	<i>Parts</i>	<i>Typical Formulation</i>	<i>Parts</i>
Neoprene	100	Mill Mix	
Magnesium oxide	4-8	Neoprene AD	100
Zinc oxide	5	Magnesium oxide	8
Antioxidant	2	Zinc oxide	5
Resins	as required	Antioxidant	2
Solvents	as required		
		Churn Mix	
		Milled stock	115
		<i>t</i> -Butyl phenolic resin	45
		Water	1
		Toluene/Hexane/Acetone	640
		(2/4/4 by volume)	



**Table 3. Properties of DuPont Neoprene Types Used in Solvent Adhesives.**

<i>Type of Neoprene</i>	<i>Characteristics</i>	<i>Specific Gravity</i>	<i>Rate of Crystallization</i>	<i>Grade</i>	<i>ML 1 + 4 at 100°C (212°F)</i>	<i>5% Solids in toluene, cps</i>
AC	General purpose elastomer with fast bond strength development, good stability and cohesive strength.	1.23	Very fast	Soft	*	31-45
				Medium	*	46-63
				Hard	*	64-100
AD	General purpose elastomer with fast bond strength development and good cohesive strength. Provides better viscosity stability than Neoprene AC.	1.23	Very fast	AD10	*	25-34
				AD20	*	35-53
				AD30	*	54-75
				AD40	*	76-115
AD-G	Similar to Neoprene AD but gives smoother, less stringy solutions and longer pot-life in isocyanate cured systems.	1.23	Very fast		*	28-46
AF	Very slow-crystallizing, room-temperature-curing elastomer. Bond strength development and hot strength are superior to Neoprene AC and AD.	1.23	Very slow		*	145-275 <sup>a</sup>
AG	High gel elastomer which gives thixotropic solutions with good application properties even at high solids content.	1.23	Does not crystallize		> 80	*
AH	Acrylic copolymer of chloroprene which forms colloidal dispersions in hydrocarbon solvents. Good application properties at high solids.	1.23	Does not crystallize		*	< 175 <sup>b</sup>
FB	High viscosity, fluid elastomer.	1.23	Slow		*	500,000-1,300,000 <sup>c</sup>
GN	Sulfur-modified elastomer with low cohesive strength and fast cure rate at room temperature.	1.23	Slow		44-65	*
GNA	Similar to Neoprene GN but contains a staining antioxidant.	1.23	Slow		41-61	*
GRT	Similar to Neoprene GN but with a very slow crystallization rate.	1.23	Very slow		36-55	*
W	General purpose elastomer with good tack. Lower cohesive strength than Neoprene AC or AD.	1.23	Slow		42-51	*
WHV	Similar to Neoprene W.	1.23	Slow	WHV-100 WHV	90-105 106-125	* *
WHV-A	Similar to Neoprene WHV but designed specifically for adhesives. Gives better resistance to phasing and more reproducible solution viscosity.	1.23	Slow		*	52-85
WRT	Similar to Neoprene W but with very slow rate of crystallization.	1.25	Very slow		41-51	*

\*Not sold to this specification.

<sup>a</sup>Viscosity at 20% solids in a milled adhesive formulation.<sup>b</sup>Viscosity at 40% solids in a dispersion.<sup>c</sup>Viscosity of fluid polymer at 50°C (122°F).

shoe industry, Neoprene AD-G is generally grafted with methyl methacrylate using a compound and procedure similar to that shown in Table 4. The resulting graft polymer has very good adhesion to plasticized PVC, EVA sponge, thermoplastic rubber, and other difficult-to-bond substrates. Further information on the graft procedure can be found in Ref. 2. The principal use of graft adhesives is in isocyanate-crosslinked cements for shoe sole attachment. Neoprene AD-G differs from standard Neoprene AD in that it provides better brushability at equal viscosity and solids content and a longer pot life in two-part systems.

Adhesives based on Neoprene AF, a reactive copolymer of chloroprene and methacrylic acid, are characterized by faster bond strength development (Fig. 1), increased heat resistance, and better resistance to phasing than the fast-crystallizing types. However, because of its reactivity, the use of Neoprene AF requires special attention to processing, compounding, and raw polymer inventory control. If it is substituted directly into a formulation based on Neoprene AC or AD, the results may be disappointing.

The improved bond strength development and hot strength of Neoprene AF results from the interaction of its polymer carboxyl functionality with metal oxides. Its crystallization

rate is very slow and plays no significant role in cohesive strength development.

In compounding Neoprene AF adhesives the polymer interaction with metal oxides must be considered. Variables which are important include resin type, solvent system, water content, polymer heat history and the order of addition of compounding ingredients. A typical Neoprene AF formulation is shown in Table 5. A comparison of the bond properties of Neoprene AF and Neoprene AD is shown in Table 6.

Brief milling of Neoprene AF, on a cool mill, is suggested to break down a light, gel-like association which builds up as the polymer ages and prevents preparation of a smooth solution under low shear conditions. Overmilling (past five minutes) will lead to increased solution viscosity and poor solution stability.

Neoprene AG is a gel polymer which exhibits a high degree of thixotropy and provides improved application properties in both low viscosity sprayable adhesives and in high solids, high viscosity mastics. Mastics based on Neoprene AG have a nonstringy, buttery consistency and can be easily applied by troweling or extruding. Because they are highly thixotropic, they resist slump after application.

Neoprene AG is often blended with Neoprene WHV-A or Neoprene AC or AD to adjust mastic properties. Blends with Neoprene AC or AD give increased shear strength but extrude less easily and provide less slump resistance. Blends with Neoprene WHV-A decrease

**Table 4. Adhesives Based on Graft Polymers of Neoprene and Methyl Methacrylate.**

<i>Formulation</i>	<i>Parts</i>
Neoprene AD-G	100
Methyl methacrylate <sup>a</sup>	100
Benzoyl peroxide (50% dispersion) <sup>b</sup>	1
Antioxidant <sup>c</sup>	2
Toluene	472
Methyl ethyl ketone	118

**Procedure:**

1. Slowly heat solution of Neoprene AD-G, methyl methacrylate, toluene, and MEK in a closed reactor vessel to 60°C (140°F).
2. Add benzoyl peroxide to initiate polymerization.
3. Continue heating to 80°C (176°F). React at 80°C (176°F) for 2-8 hours.
4. Add antioxidant to terminate the polymerization.

<sup>a</sup>Grade H-112 from DuPont.

<sup>b</sup>Cadox BFF-50 from Noury Chemical.

<sup>c</sup>Wingstay L from Goodyear.

**Table 5. Neoprene AF Formulation**

<i>Formulation</i>	<i>Parts</i>
<b>Mill Mix</b>	
Neoprene AF (5 min break down)	100
Antioxidant	2
Magnesium oxide	8
Zinc oxide	5
<b>Churn Mix<sup>a</sup></b>	
Milled stock	115
<i>t</i> -Butyl phenolic resin	40
Water	1
Solvent	610 <sup>b</sup>

<sup>a</sup>Gelation can be minimized if the milled stock is added to a pre-dissolved resin and solvent solution.

<sup>b</sup>A blend of aromatic/aliphatic/oxygenated solvents is used. Approximately 20% of an oxygenated solvent is required for good solution stability.

**Table 6. Adhesive Properties: Neoprene AF vs. Neoprene AD.<sup>a</sup>**

<i>Adhesive Properties</i>	<i>Neoprene AF Pulled at R.T.</i>	<i>Neoprene AD Pulled at R.T.</i>	<i>Neoprene AF Pulled at 100°C (212°F)</i>	<i>Neoprene AD Pulled at 100°C (212°F)</i>
<b>Bond Strength Development,</b> Canvas/canvas peel, pli				
After 1 hr at R.T.	16	1		
After 2 hr at R.T.	20	2		
After 4 hr at R.T.	24	4		
After 6 hr at R.T.	26	8		
After 1 day at R.T.	32	32		
After 7 days at R.T.			13	3
<b>Adhesion to Various Substrates</b> After 14 days at R.T., pli				
Canvas	39	38	18	1
Aluminum	30	26	16	0.5
Maple	30	21	15	0.5
Decorative laminate	38	37	13	1
Composition soling	40	37	7	0.5
Stainless steel	28	25	15	1

<sup>a</sup>Using formulation shown in Table 5.

cost and increase tack at the expense of both application properties and shear strength. A comparison of Neoprene AG and AC in a mastic formulation is presented in Table 7.

Mastics based on Neoprene AG can be prepared in a sigma blade mixer from polymer which has first been preswollen in solvent. Milling is not required to produce smooth, non-stringy products.

In low solids formulations, the gel structure of Neoprene AG provides improved spray performance compared to products based on other Neoprene types. Properly formulated compositions can be sprayed in uniform patterns with no cobwebbing at low atomization pressures (<70 psi). Preferred solvent systems for sprayable compositions fall in the range of 3.5–5.5 hydrogen bonding index and 7.5–9.8 solubility parameter. A low atomization pressure, sprayable adhesive formulation is presented in Table 8. To obtain the best application properties, either milling or high shear processing is required to break up loose gel agglomerates in the polymer.

Neoprene AG is compounded like Neoprene AC and AD. However, formulations based on Neoprene AG give lower ultimate cohesive strength, specific adhesion, and open tack time than the fast crystallizing types. For this reason, Neoprene AG is often blended with Neo-

prene AC or AD to lengthen tack time and to obtain better substrate wetting and subsequently higher peel strength.

Neoprene AH is an acrylic copolymer of chloroprene which forms a colloidal dispersion when peptized in aliphatic solvents. The use of aliphatic solvents alone, without toluene or ketones, offers the advantages of low cost, acceptability under Rule 66, and the capability to bond substrates such as polystyrene which are sensitive to aromatic or ketone solvents.

The stability of the dispersion is due to steric stabilization of the acrylic portion of the polymer in the solvent. The dispersion nature of Neoprene AH systems allows the formulation of high solids, low viscosity adhesives with excellent application properties. The sprayability of formulations with solids contents as high as 50% (2500 cps) is good, exhibiting none of the cobwebbing normally seen in Neoprene systems. The open tack time of Neoprene AH is shorter than that of the other types, generally around fifteen minutes.

The preparation of a stable dispersion is the key requirement to obtaining a stable adhesive system. Neoprene AH should be peptized in a low-naphthenic, aliphatic hydrocarbon solvent. The suggested peptization system consists of the peptizing agent tetraethylthiuram disulfide activated by Vanax 552 (R. T. Vanderbilt), as

**Table 7. Neoprene Mastic Compound.<sup>a</sup>**

<i>Formulation</i>	<i>Parts</i>	
Neoprene	100	
Antioxidant	2	
Magnesium oxide	4	
Zinc oxide	5	
Treated calcium carbonate <sup>b</sup>	100	
Ethylene glycol	2	
<i>t</i> -Butyl phenolic resin	20	
Terpene phenolic resin	15	
Hexane/MEK/Toluene to 65% solids (5/3/2 by weight)		
<i>Polymer Type</i>	<i>Neoprene AG</i>	<i>Neoprene AC</i>
Slump <sup>c</sup> after 20 min, inches	0.0	2.9
Extrusion Rate, <sup>d</sup> g/5 sec At R.T.	70	19
Shear strength <sup>e</sup> at R.T., Plywood/plywood, psi		
After 3 days at R.T.	150*	140
After 7 days at R.T.	240*	250*
After 14 days at R.T.	240*	320*
Shear strength <sup>e</sup> at R.T., Maple/maple, psi		
After 3 days at R.T.	40	38
After 7 days at R.T.	140	156
After 14 days at R.T.	160	250

\*Indicates wood failure. All other failures were adhesive.

<sup>a</sup>Ref. 7

<sup>b</sup>Omya BLH, OMYA, Inc.

<sup>c</sup>Flow measured on 1.5 in. drain; 3/8-in.-thick adhesive sample on a vertical surface.

<sup>d</sup>Extruded at 50 psi, 1/8-in. orifice

<sup>e</sup>1/16-in. glueline tested at 1/2 in./min.

is shown in the adhesive formulation presented in Table 9. The dispersion should be prepared under shear, the degree of which affects the time to disperse and the final viscosity. The time to make a 40% dispersion varies from about 30 minutes in a high-shear Silverson

Mixer to a few hours in a Struthers-Wells churn.

Other Neoprene polymers which find use in solvent adhesives are Neoprene WHV-A, Neo-

**Table 8. Sprayable Formulation Based on Neoprene AG.**

<i>Formulation</i>	<i>Parts</i>
Mill Mix	
Neoprene AG	100
Antioxidant	2
Magnesium oxide	8
Zinc oxide	5
Churn Mix	
Milled stock	115
<i>t</i> -Butyl phenolic resin	40
Water	1
MEK/Cyclohexane (4/1 by volume)	620

**Table 9. Neoprene AH Formulation.**

<i>Formulation</i>	<i>Parts</i>
Disperse by churn mixing:	
Neoprene AH	100
Heptane	150
Tetraethylthiuram disulfide	0.5
Vanax 552 <sup>a</sup>	0.5
Add the following to the above dispersion:	
<i>t</i> -Butyl phenolic resin	20-40
Tackifier	0-20
Magnesium oxide	2
Zinc oxide	4
Antioxidant	2
Water	1

<sup>a</sup>Piperidinium pentamethylene dithiocarbamate, R. T. Vanderbilt

prene GN and Neoprene FB. Both Neoprene FB and Neoprene GN are sulfur-modified types which can be mechanically or chemically peptized to reduce molecular weight if desired. Both exhibit a faster cure rate than the fast crystallizing types and can be used in formulations which are intended as either two-part adhesives or curable compositions. Neoprene FB differs from the other solvent types in that it is a viscous, pourable fluid at 50°C (122°F) which can be used in the formulation of 100% solids caulks and sealants. Neoprene WHV-A, a member of the W-family of polymers, is a slow-crystallizing, high molecular weight polymer which is generally used in blends with lower molecular weight crystallizing types to increase solution viscosity. As a minor component in such blends, it will not have too adverse an effect on bond strength development.

### Antioxidants

The presence of a good antioxidant is essential in all adhesive formulations for adequate protection against oxidative breakdown and acid tendering of substrates. Octylated diphenylamine antioxidants, such as Agerite Stalite S (R. T. Vanderbilt), afford the best protection but can be used only in applications where staining is of no concern. If discoloration cannot be tolerated, a nonstaining hindered bisphenol such as Wingstay L (Goodyear) or Antioxidant 2246 (American Cyanamid) should be used. Two parts of an antioxidant is generally sufficient. For very demanding applications higher amounts may be advisable.

The hindered bisphenol antioxidants, while useful for minimizing staining, can present problems in some formulations. For example, milled stocks containing some hindered bisphenols such as Santowhite Crystals (Monsanto) have relatively short bin stability. On aging, for as little as one week at 38°C (100°F), the stock may not make a smooth solution. If the stocks are dissolved within two or three days of milling, no problems are normally encountered. Antioxidant 2246 (American Cyanamid) has been known to create color problems: a pink discoloration in latexes, a bluish or blue-green discoloration in some solvent systems, particularly those based on chlorinated solvents.

### Metal Oxides

Metal oxides serve several functions in Neoprene adhesives as shown below:

#### Role of Metal Oxides

Acid acceptor	ZnO, MgO
Scorch retarder	MgO
Curing agent	ZnO, MgO
<i>t</i> -Butyl phenolic resin reactant	MgO

The prime function is that of an acid acceptor. Small amounts of HCl are released as Neoprene films age. The HCl must be absorbed by the adhesive to prevent substrate degradation. This is particularly important when the adhesive is applied to acid-sensitive materials such as rayon or cotton. Both magnesium oxide and zinc oxide function as acid acceptors. A combination of the two is more effective than either alone.

Magnesium oxide serves a second function as a processing stabilizer. It is mill mixed with Neoprene before adding zinc oxide to retard scorch during processing.

Metal oxides also act as curing agents in adhesive films. Zinc oxide is the most effective, leading to increased strength as the bond line ages. At higher levels (20–40 phr) magnesium oxide also is effective, particularly if the bond is briefly exposed to elevated temperatures.

As will be discussed in the section on resins, metal oxides also react in solution with *t*-butyl phenolic resins. The reaction product, an infusible metal resinate, increases the heat resistance of adhesive films. Although oxides of calcium, lead, and lithium also exhibit reactivity, magnesium oxide is the most useful and widely used reactant.

Generally about five parts of zinc oxide and four to eight parts of magnesium oxide are used in adhesives with 40 phr resin. Four parts of the magnesium oxide are included to act as an acid acceptor and to retard scorch. An additional four parts are included as a resin reactant if the adhesive system contains a *t*-butyl phenolic resin.

There has been some interest in reducing or eliminating metal oxides in adhesive films in order to produce clear adhesives. The amount of magnesium oxide should not be reduced below that required to react fully with the *t*-butyl

phenolic resin. Epoxy resins and zinc resinate have been used in place of zinc oxide as acid acceptors, but are not as efficient. Some sacrifice in tendering resistance must be acceptable, therefore, if a clear adhesive is desired. At least 2 phr of an antioxidant is essential to obtain the best possible tendering resistance.

## Resins

The choice of which resin to use in a given solvent adhesive application is of great importance. Resins serve to improve specific adhesion and autohesion, obtain longer tack retention and increase hot cohesive strength. The most widely used family of resins are the *para-tertiary butyl phenolics*. These resins give much higher heat resistance than other types of resins with similar melting points. This high heat resistance is due to their reactivity with the magnesium oxide present in Neoprene adhesive systems. The magnesium oxide resinate or resin

salt is infusible. It has no melting point, and decomposes above 200°C (392°F). It therefore reduces the thermoplasticity of the system, providing good bond strength up to 80°C (176°F) or higher in properly formulated adhesives. The resinate also increases adhesive bond strength development by accelerating solvent release. A comparison of *t*-butyl phenolics with other resins in Neoprene AD and AH adhesives is shown in Tables 10 and 11.

The *t*-butyl phenolic resins are generally used at levels between 35 and 50 phr. The optimum level for most adhesive applications is 40–45 phr, which provides a good balance of tack and heat resistance. Lower levels are useful when the required level of adhesion is relatively low and a soft glue line is desirable. Higher levels of resin are used when the demand for good adhesion is high, such as in metal-to-metal bonding. The variation in open tack time and hot bond strength with increasing *t*-butyl phenolic resin content is shown in Fig. 4.

**Table 10. Effect of Resin Type on Heat Resistance.**

	Base Compound				Parts			
	Neoprene AD-20 (10 min breakdown)				100			
	Magnesium oxide				4			
	Zinc oxide				5			
	Antioxidant				2			
	Resin				as shown			
	Water				1			
	Hexane				100			
	Toluene				400			
Resin Selection	A	B	C	D	E	F	G	H
<i>t</i> -Butyl phenolic resin <sup>a</sup>	46	—	33	33	—	33	—	33
Hydrocarbon resin	—	25	22	—	—	—	—	—
Rosin ester	—	—	—	22	—	—	—	—
Terpene	—	—	—	—	65	22	—	—
Terpene phenolic	—	—	—	—	—	—	65	22
Solids content, %	24	21	25	25	26	25	26	25
Canvas/canvas bond strength at R.T., pli <sup>b</sup>								
After 1 day at R.T.	31 A	10 C	12 C	14 C	10 C	18 C	16 C	32 C
After 7 days at R.T.	46 A	25 A	36 A	42 A	4 F	23 A	30 A	40 A
Canvas/canvas bond strength at 80°C (176°F), pli								
After 7 days at R.T.	5.5	0.5	0.5	0.5	0.5	0.5	0.5	2.0

<sup>a</sup>Magnesium oxide reacted.

<sup>b</sup>A = adhesive failure, C = cohesive failure, F = failure between films.

**Table 11. Effect of Resin Type on Neoprene AH Hot Bond Strength.<sup>a</sup>**

Adhesive Properties	Rosin Ester	Terpene Phenolic	<i>t</i> -Butyl Phenolic Resin	
			Low Reactivity	High Reactivity
Bond strength after 1 day at R.T., pli				
Tested at R.T.	5.4 C	9 C	20 C	21 C
Bond strength after 7 days at R.T., pli				
Tested at R.T.	8 C	21 C	34 A	42 A
Tested at 60°C (140°F)	—	—	18 C	28 C
Tested at 80°C (176°F)	—	—	6 C	16 C
Tested at 100°C (212°F)	0.3 C	0.8 C	2.5 C	7 C
Open tack time, paper to steel, min.	60	16	10–14	4–8

<sup>a</sup>Based on formulation in Table 9 with 40 phr of resin.

C = cohesive failure, A = adhesive failure

Approximately 10 parts of magnesium oxide are required to react completely with 100 parts of resin. This is equivalent to 4 parts of magnesium oxide in a solution containing 100 parts of Neoprene and 40 of resin. The reaction takes place at room temperature and requires the presence of water as a catalyst. Although there is generally enough water in the solvent system to ensure reactivity, it is common practice to add 1–2 parts of water by weight of resin to the formulation.

The solvent system used has a strong effect on the rate of the magnesium oxide and resin reaction. In toluene the reaction is very fast, reaching completion in one hour. In polar sol-

vents the reaction proceeds more slowly, as shown in Table 12. In cases where the solvent system contains a high percentage of polar solvents, it may be advisable to prereact the resin in the nonoxygen-containing component of the blend to ensure the reaction reaches completion.

The use of *t*-butyl phenolic resins is essential in compounding Neoprene AF for maximum viscosity stability and the best balance of adhesion properties. This class of resins helps stabilize the carboxyl functionality of Neoprene AF in solution. The magnesia-tertiary butyl phenolic resin complex reacts with the polymer carboxyl groups as shown in Fig. 5, preventing gelation of the polymer with the metal oxide alone. Increased resin levels are particularly effective in stabilizing compounds which are formulated for maximum heat resistance and contain high levels of magnesium oxide.

Neoprene adhesives containing metal oxides and *t*-butyl phenolic resins may separate on standing into a clear upper layer and a lower layer of flocculated metal oxides. This separation, called *phasing*, may occur in days or months. Once an adhesive has phased, it must be agitated before use to obtain full utility of the metal oxides.

It is theorized that phasing is due to insufficient dispersion stability of the metal oxides, resulting from low molecular weight portions in commercial resins which are not large

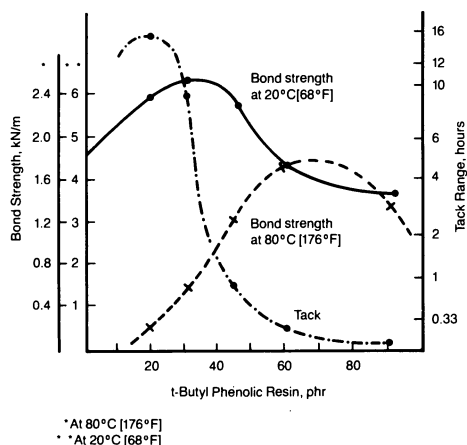


Fig. 4. Effect of *t*-butyl phenolic resin level on open tack time and heat resistance.

**Table 12. Effect of Solvent Blend on the Rate of the Magnesium Oxide/Resin Reaction.<sup>a</sup>**

Solvent	Reaction Time, hr	Ash Content of Reacted Resin, % <sup>b</sup>	Melt or Decomp. Temp. of Reacted Resin, °C (°F)
Toluene	1	6.5	250 (482) D <sup>c</sup>
	24	6.8	258 (496) D
	96	6.7	252 (486) D
Tol/ethyl acetate/hexane (1/1/1 by weight)	24	6.9	255 (491) D
	96	7.1	255 (491) D
Toluene/hexane (1/1 by weight)	24	6.9	264 (507) D
Hexane	24	7.0	252 (486) D
Acetone	24	0.4	181 (358) M
Hexane/MEK (1/1 by weight)	24	0.4	125 (257) M
	48	2.9	130 (266) M
	72	6.1	226 (439) M
	96	6.2	224 (435) M

<sup>a</sup>Formulations contained 1 phr water and about 10 phr MgO per 100 phr resin.

<sup>b</sup>>6% ash and decomp. temp >250°C (482°F) indicates the reaction has gone to completion.

<sup>c</sup>D = decomposed, M = melted.

enough to prevent particle attraction and agglomeration when adsorbed on the metal oxide surface. Commercial *t*-butyl phenolic resins with a number average weight of 900–1200 can contain as much as 10–15% by weight of material having a molecular weight less than 500. By increasing the average molecular weight of commercial *t*-butyl phenolic resins from 900 to 1600 and fractionating out the low molecular weight portion, DuPont workers were able to produce cements that did not phase. A series of experiments conducted by a team of workers at Hitachi Chemical Co.<sup>4</sup> confirmed this and demonstrated further that phasing was caused primarily by various dialcohols such as *p*-*tert*-butyl phenol dialcohol (BPDA). The DuPont

and Hitachi work led to the development of so-called *nonphasing resins* (i.e., Schenectady's SP-154, and Union Carbide's CK-1636). In addition to resin choice, the formulator interested in minimizing phasing must also consider the type of Neoprene, solvent system, solids content, milling time, etc.

*Terpene phenolic* resins, such as Schenectady's SP-560 or Occidental's Durez 12603, are also often used in Neoprene adhesives. They are nonreactive and thermoplastic in nature and so provide longer open tack time and a softer glue line than the *t*-butyl phenolics, but offer less hot cohesive strength. Terpene phenolic resins are often used in combination with a *polyisocyanate* curing agent, such as Bayer's Desmodur RF, in a two-part adhesive system to obtain better hot bond strength.

*Other resins* which find use as tackifiers for Neoprene include polyterpene resins, hydrogenated wood rosins, rosin esters, and coumarone-indene resins. Chlorinated rubber is used to promote metal adhesion and as an ingredient of two-component adhesives. Poly- $\alpha$ -methyl styrene is used to obtain better specific adhesion to thermoplastic rubber. The compatibility of Neoprene with resins and other polymeric materials is detailed in Ref. 11.

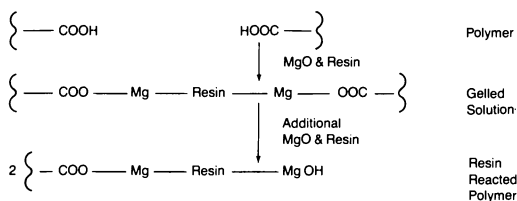


Fig. 5. Magnesia and tertiary butyl phenolic interaction with polymer acid. (The resin should be added before or at the same time as the MgO to prevent gelation during mixing.)



## Fillers

Fillers find limited use in Neoprene adhesives. They are included primarily to reduce cost in high solids mastics. Conventional fillers such as clay and calcium carbonate are used effectively at levels as high as 250 phr in some mastic applications.

The optimum filler concentration in Neoprene AG based mastics depends on the filler used. Maximum bond strength is obtained with fillers of low particle size ( $\sim 5$  micron) and intermediate oil absorption (30 g/100 g filler); mastic extrusion rate and slump increase with decreasing filler absorption, almost independently of filler particle size.<sup>6</sup> Increasing the level of the treated calcium carbonate in Table 7 above 100 phr causes the mastic to slump and the impact resistance to decrease.

In general, fillers reduce the specific adhesion and cohesive strength of adhesive films. For these reasons, they are rarely used in low solids contact adhesives. In some formulations, e.g., Neoprene-terpene phenolics, the inclusion of a fine particle size reinforcing silica such as HiSil 233 (PPG Industries) will increase film strength. This effect is lost in formulations using reacted magnesium resinate systems.

## Curing Agents

The heat resistance of Neoprene cements can be increased by compounding with a variety of curing agents such as thiocarbanilide, mixtures of sulfur with Vanax 808 or 833 (R.T. Vanderbilt), triethyl trimethylene triamine, and monomeric or polymeric isocyanates. Room temperature cure rates with these curing agents are slower with the A-types of Neoprene than with the G-types. Such systems are not generally employed in the U.S. because heat-reactive *t*-butyl phenolic resins provide equivalent or better heat resistance. Solutions containing curing agents are also relatively unstable and hence two-package systems are required. In other countries, however, isocyanate-cured Neoprene systems are popular, particularly in the shoe industry.

In Neoprene AF systems, metal oxides act as rapid room temperature curatives because of their reactivity with the polymer carboxyl functionality. When properly compounded, the car-

boxyl functionality is stable in solution; thus one-part curing cements are possible.

## Solvents

Solvent choice affects adhesive viscosity, bond strength development, open time, cost, and to some degree ultimate strength. Trisolvant blends are generally used, consisting of varying amounts of aromatic, aliphatic and oxygenated solvents such as ketones and esters. In cases where nonflammable systems are required, chlorinated solvents such as 1,1,1-trichloroethane are employed.

A graphical method can be used to predict the utility of solvent blends in adhesives based on Neoprene. It is based on using the solubility parameter ( $\delta$ ) and the hydrogen bonding index ( $\gamma$ ) of each constituent solvent to predict that of the blend. The  $\delta$  and  $\gamma$  of blends are additive according to their volume proportions.

Once the solubility parameter and hydrogen bonding index of the blend has been determined, the blend can be positioned on the chart shown in Fig. 6. Solvents or blends which fall within the kidney shaped area will yield smooth, free-flowing solutions with all solvent grade types except Neoprene AH. Those which fall outside the kidney shape will not dissolve Neoprene. If a particular solvent blend falls in the shady area it may or may not be suitable depending on the amount of true solvent (e.g., toluene) in the blend.

Current regulations governing the use of solvents in adhesives vary from state to state and the adhesive formulator will need to assure himself that his products comply with both federal and local regulations. Table 13 indicates the restrictions imposed by Rule 66.

The evaporation rates of common solvents are also shown in Table 13. Because the open tack time of an adhesive is partially dependent on the evaporation rate of the solvent system, this property can be controlled to some degree through solvent selection. Small percentages of xylene ( $< 5\%$ ) are often added to increase open time, particularly in consumer products. In addition, the evaporation rates of the various components of a blend must be taken into account. If the better solvent is the slowest to evaporate, the adhesive will retain tack longer.

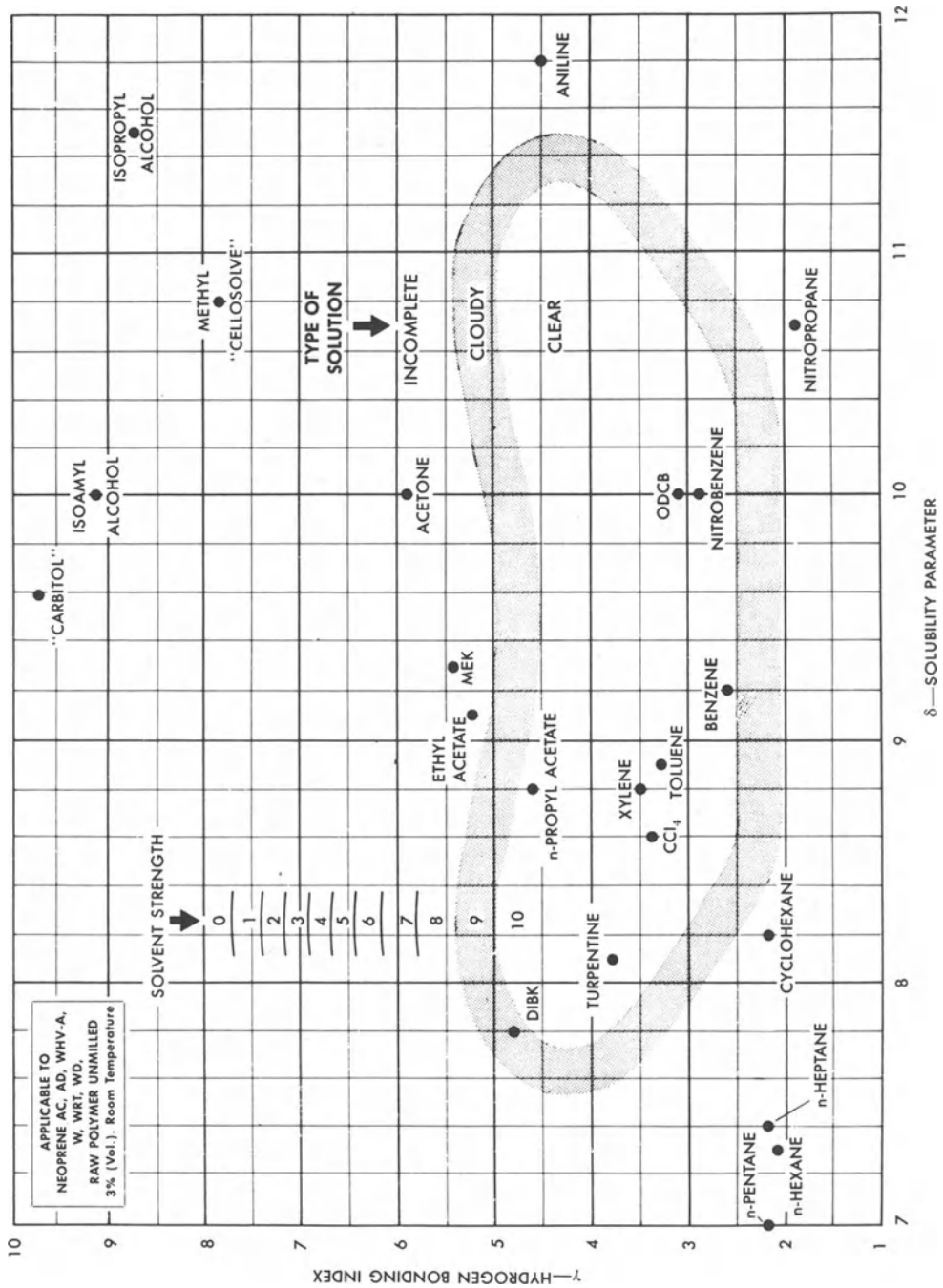


Fig. 6. Solvent strength chart (Ref. 9).

**Table 13. Properties of Commonly Used Neoprene Solvents.<sup>d</sup>**

<i>Solvent</i>	<i>Molecular Wt</i>	<i>Solubility Parameter</i>	<i>Hydrogen Bonding Index (HB)</i>	<i>Relative Evaporation Rate<sup>a</sup></i>	<i>Flash Point °F<sup>b</sup></i>	<i>Max. Allowable Concentration ppm<sup>c</sup></i>	<i>Viscosity, cps at 20°C (68°F)</i>	<i>Restriction Rule 66</i>
Acetone	58.08	10.0	5.9	1160	15	1000	0.35	None
Cyclohexane	84.16	8.2	2.2	720	40	300	1.06	None
Ethyl acetate	88.10	9.1	5.2	615	45	400	0.44	None
Heptane	100.20	7.4	2.2	386	25	500	0.42	None
Hexane	86.17	7.3	2.1	1000	-25	500	0.29	None
Isopropyl alcohol	60.09	11.5	8.7	300	70	400	2.41	None
Methyl ethyl ketone	72.10	9.3	5.4	572	35	200	0.42	None
Pentane	72.15	7.0	2.2	2860	< -50	500	0.24	None
Toluene	92.13	8.9	3.3	240	44	100	0.59	20%
Xylene	106.16	8.8	3.5	63	80	100	0.69	8%
V.M. & P Naphtha	*	7.6	2.5	275	48	500	*	None

<sup>a</sup>n-Butyl acetate = 100.<sup>b</sup>Cleveland Open Cup Method.<sup>c</sup>Maximum allowable concentration in air where men work 8 hr/day "Dangerous Properties of Industrial Materials", 4th ed., N. (. Sax, Van Nostrand Reinhold, New York, 1975.)<sup>d</sup>Ref. 10.

\*Mixture of various hydrocarbons—no definable molecular weight or viscosity.

If, on the other hand, it evaporates the most quickly, cohesive strength will develop more rapidly.

Solvent choice also affects application properties. True solvents, such as toluene or 1,1,1-trichloroethane, give stronger solutions which tend to be more stringy and cobweb when sprayed. Improved application properties are obtained by using a blend which falls closer to the shady area of the kidney shaped solvent diagram. For example, sprayable adhesives are generally based on fast-evaporating solvent blends which fall in the upper left quadrant of Fig. 6.

A small amount of water, about 1 phr, is often added to catalyze formation of the magnesium oxide/resin reaction product and to improve the viscosity stability of Neoprene AF adhesives. However, excess water reduces the hot cohesive strength of the adhesive. Therefore, levels less than 3 phr are generally used.

### Adhesive Processing

The procedures used to prepare Neoprene adhesive cements can affect end use properties such as hot cohesive strength and sprayability. Techniques used to prepare cements include milling, direct dissolving, and direct dissolving

plus high shear refining. A brief description of each follows.

**Milling.** The polymer is broken down on a two-roll rubber mill prior to dissolution. To be effective, milling should be carried out on a tight, cool mill—tight to increase the rate of shear, cool for the greatest degree of chain scission. Neoprene can go through three phases on a mill depending upon its temperature: elastic phase <71°C (160°F), granular phase 71–93°C (160–200°F), plastic phase >93°C (200°F). Optimum breakdown and dispersion occur in the elastic phase.

The metal oxides and antioxidant may be added to the polymer as it is being broken down on a mill. The masterbatch is then dissolved with any other compounding ingredients. This procedure provides better dispersion of the metal oxides, which improves resistance to phasing in the final adhesive. The antioxidant and magnesium oxide should be incorporated before the zinc oxide to retard scorch during processing.

Milling aids in producing smooth, non-stringy cements by selectively breaking down the high molecular weight fraction of the polymer. In applications requiring sprayable adhe-

sives, milling is recommended in order to obtain the best application properties. Milling also increases penetration into porous substrates and decreases solution viscosity and early hot bond strength.

For example, milling Neoprene AC for 5 min [stock temperature  $\sim 50^{\circ}\text{C}$  ( $122^{\circ}\text{F}$ )] reduces initial  $100^{\circ}\text{C}$  ( $212^{\circ}\text{F}$ ) peel strength from 7 lb/in. to less than 1 lb/in. After a bond aging period of one month, both have 12 lb/in. peel strength at  $100^{\circ}\text{C}$  ( $212^{\circ}\text{F}$ ) as a result of partial curing with zinc oxide.

The effect of milling on the Mooney viscosity of Neoprene AC, Neoprene AD and Neoprene AF is shown in Fig. 7. Neoprene AF does not break down to the same extent as the fast crystallizing types. Milling, therefore, does not have as large an effect on the solution viscosity of Neoprene AF cements. Because the bond strength development of Neoprene AF is largely due to reaction with zinc oxide, it is not significantly affected by milling.

The granulators, dicers, and shredders used in the rubber industry are also employed in the preparation of mill-mixed adhesive stocks. They are used to precut mill stock prior to charging it to the churn to increase the rate of solution.

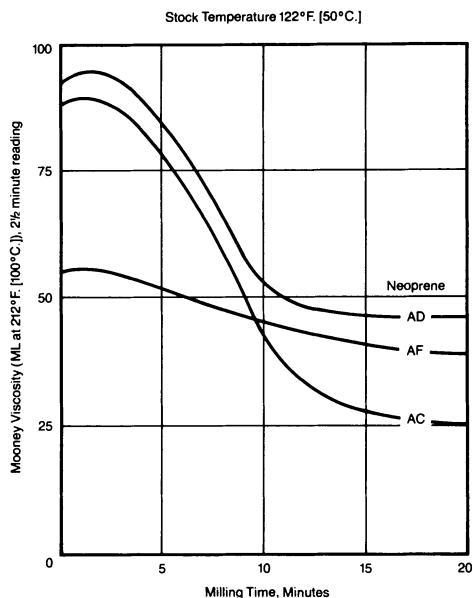


Fig. 7. Effect of milling on Mooney viscosity.

**Direct Dissolving.** The polymer chips are dissolved with the other compounding ingredients in either high or low shear mixing equipment. This method is more economical than the previous one because milling equipment and the manpower required to operate it are not required. Direct addition of dry ingredients to solvent or to a solution of Neoprene is not recommended, however, unless the blending equipment is capable of creating a smooth dispersion of these materials. With a slow-speed churn, it may be necessary to make a separate dispersion of dry ingredients in solvent by ball milling before adding them to the Neoprene solution—hence this technique is often referred to as the *slurry method*.

Dissolvers can be classified as slow-speed churns, high-speed churns, or heavy-duty mixers, depending on their relative rates of solution of stock or their energy input. Slow-speed churns may be mounted either vertically or horizontally. Typical solution time ranges from 24 to 48 hours. Those mounted horizontally may contain an agitator or they may be agitated through rotation of the churn. Horizontal churns are well suited for the production of low viscosity adhesives. Vertical churns are jacketed vessels which are agitated by paddles on a vertical shaft. Vertical churns can be used for all types of cements but are especially suited for high viscosity cements.

High-speed churns are designed to speed up the preparation of smooth cements. Because of their shearing action, they provide some polymer breakdown and resultant viscosity reduction. They generate considerable heat, so a jacketed vessel is preferred to control heat history. The heat build-up increases the rate of solution, particularly with the crystalline types because in addition to the simple temperature effect on solubility, heating decrystallizes the polymer.

High-speed churns may be shearing disk type or propeller type. The latter, typified by the Struthers Wells churn, consists of two opposed propellers positioned in the sides of a closed cylindrical vessel, slightly off horizontal, one on top of the churn, the other at the bottom. Shearing disk churns usually have variable speed control and differ from one another in the

design of the flat disk at the end of the shaft. Examples of such dissolvers include the Hockemeyer Disperser and the Cowles Dissolver. Solution time for high-speed churns ranges from 3 to 12 hours.

Heavy duty mixers or kneaders are adapted to the manufacture of heavy doughs or troweling compounds which have viscosities too high for practical processing in the equipment discussed above. These are high-energy internal mixers utilizing counter-rotating rotors like a Banbury, with sigma- or Z-shaped blades. By careful addition of solvent, a smooth cement can be prepared in two hours or less. Too rapid addition of solvent will cause the compound to "liver" and an abnormally long period of time will be required for solution.

**Direct Dissolving plus High Shear Refining.** This procedure combines many of the attractive features of milling and nonmilling. It involves subjecting a previously dissolved adhesive to high shear for several minutes in equipment such as a Ross mixer emulsifier. The high shear refining step breaks down the high molecular weight fraction of the polymer, yielding nonstringy adhesives and better metal oxide dispersion without the sacrifice in hot strength associated with milling. The adhesive

viscosity obtained using this procedure is intermediate between that of milled and unmilled adhesives.

In the past 8–10 years, many adhesive manufacturers have turned to high shear processing as a means of attaining adhesives with a smooth, mill-like consistency without the required investment in capital and manpower. Some use a high shear refining step as described here while others speed up mixing time by charging all ingredients directly to the mixer emulsifier unit. A comparison of milling, direct dissolving, and dissolving plus high shear refining is shown in Table 14.

### End Uses

Areas where Neoprene solvent cement is popular include adhesives for bonding high pressure plastic laminates, automotive adhesives, adhesives for the construction industry and shoe adhesives.

Shoe adhesives have traditionally been a large market for Neoprene, particularly for the permanent attachment of shoe soles. However, traditional Neoprene contact cements do not give adequate adhesion to plasticized PVC, a synthetic material for shoe uppers which has grown in significance in recent years, because

**Table 14. Effect of Adhesive Processing on Viscosity and Creep Resistance of Neoprene AD Adhesive.<sup>a, b</sup>**

<i>Processing</i>	<i>5 min Mill Breakdown</i>	<i>Churn Mix</i>	<i>Churn Mix Plus High Shear<sup>c</sup></i>
Brookfield Viscosity, cps	220	1220	1050
Creep at 50°C (122°F) after 120 min with 5 lb weight, Canvas/canvas Bonds, Inches separation <sup>d</sup>			
1 day bond aging	1.7 C	0.8 C	0.7 C
5 days bond aging	0.5 C	0.3 C	0.3 C
Open time, chipboard to for- mica Bonds Assembled After <sup>e</sup>			
30 min	4	5	5
60 min	2	5	3
90 min	0	5	0
120 min	0	5	0
180 min	0	0	0

<sup>a</sup>Ref. 12

<sup>b</sup>Neoprene AD-30 adhesive with 40 phr *t*-butyl phenolic resin.

<sup>c</sup>3 min in homogenizer.

<sup>d</sup>C = Cohesive failure.

<sup>e</sup>Values 1 through 5 correspond to increasing bond strength.

of plasticizer migration into the bond line. In response to a need for better adhesion, Neoprene AD-G was developed. As was discussed earlier, it is designed for grafting with methyl methacrylate at the adhesive manufacturer's facilities. The resulting graft polymer solution gives good adhesion to PVC without further compounding. For sole attachment, it is used as a two-part adhesive in combination with a polyisocyanate. The graft system also gives good adhesion to other hard to bond substrates such as EVA sponge, thermoplastic rubber and SBR. In some of these cases, small amounts of resins are used to increase specific adhesion.

Automotive uses for Neoprene adhesives also go back many years and include such things as adhering sponge insulation strips to doors and trunk and hood lids. Other applications include attachment of vinyl trim in panels and adhering vinyl landau tops to roofs. Traditional Neoprene/resin contact cements are used to bond plasticized PVC in these applications because the required adhesion level is not as great as in the shoe industry and/or a barrier film is employed.

Another large market for Neoprene adhesives is the bonding of high-pressure plastic laminates to substrates such as wood, metal, stone, etc. The contact cement enables construction personnel to make kitchen cabinets in place. Neoprene's rapid bond strength development and high ultimate strength make it feasible to install rolled edges for splash panels at the back of counters, etc. Greater and greater use of contact adhesives is also being found in factory manufactured plastic laminated panels.

In the construction industry, Neoprene finds use in a variety of jobs. Some of the larger volume applications include: adhering gypsum dry walls (wallboard) to itself in double dry wall construction, adhering faces to paper and wood core materials in flush doors and curtain wall panels, and mastics for bonding plywood flooring to joists.

### Application Methods

Neoprene adhesives are conventionally applied by spraying, curtain coating, roller coating, brushing, or extrusion (i.e., by a caulking gun). Spraying is by far the most important industrial technique, as it permits rapid laydown of ad-

hesive and minimizes drying time. The basic physical characteristics required of Neoprene adhesives for these application techniques are summarized below.

1. *Spraying.* A low Mooney, low nerve Neoprene is preferred. Milling is required for the best spray characteristics. The viscosity should be below 250 cps. The solvent blend should contain predominantly fast-evaporating solvents which individually could not dissolve Neoprene.
2. *Curtain coating.* A low Mooney, low nerve Neoprene is preferred. Milling or high shear refining improves curtain coating characteristics by reducing nerve. Viscosity should be 200–300 cps utilizing relatively slow evaporating solvents.
3. *Roller coating.* Milling or high shear refining is recommended to reduce stringiness. The viscosity should be 500–1000 cps using relatively slow evaporating solvents. The slowest evaporating solvents should be true solvents, either individually or as a blend, in order to reduce "snap-back."
4. *Brushing.* The viscosity should be around 1000 cps. Solvent system, beneficial effect of milling, etc., depends on individual application requirements.
5. *Extrusion.* A high gel, low viscosity thixotropic Neoprene is best. The ideal candidate is Neoprene AG, by itself or in blends with AC, AD or WHV-A. The solvent blend should contain predominantly fast-evaporating solvents which individually could not dissolve Neoprene.

### NEOPRENE LATEX-BASED ADHESIVES

Neoprene latexes can be categorized as anionic or nonionic. The one nonionic latex available, Latex 115, is stabilized with polyvinyl alcohol and sold at a pH of about 7.0. Ten other latexes are available which are stabilized with anionic emulsifier systems. Seven of these are commonly used in adhesives. The properties of the Neoprene latexes used in adhesive applications are summarized in Table 15 and in the following text.

Table 15. Properties of Neoprene Latex Polymers.

<i>Latex Type</i>	400	571	654	671A	735A	750	842A	115
Primary monomer	chloroprene	chloroprene	chloroprene	chloroprene	chloroprene	chloroprene	chloroprene	chloroprene
Comonomer	2,3-dichloro-1,3-butadiene	sulfur	—	—	—	2,3-dichloro-1,3-butadiene	—	methacrylic acid
Emulsifier type	potassium salt of disproportionated resin acids	principally sodium salts of resin acids	potassium salt of disproportionated resin acids	potassium salt of disproportionated resin acids	sodium salt of disproportionated resin acids	potassium salt of disproportionated resin acids	principally sodium salts of resin acids	polyvinyl alcohol
Class	anionic	anionic	anionic	anionic	anionic	anionic	anionic	nonionic
Latex characteristics:								
Percent solids	50	50	59	59	45	50	50	47
Initial pH at 25°C	12.5	12.0	12.0	12.5	12.0	12.5	12.0	7.0
(77°F), minimum								
Viscosity, cps								
Spindle 1 at 6 rpm	9	15	75	60	5	10	15	—
Spindle 1 at 30 rpm	9	15	55	45	5	10	15	—
Spindle 2 at 6 rpm	—	—	—	—	—	—	—	500
Spindle 2 at 30 rpm	—	—	—	—	—	—	—	350
Gel content	medium	high	low	medium	very low	medium	high	low
Film properties:								
Modulus at 100% elongation, MPa	1.8	0.6	0.2	0.6	0.2	0.4	0.4	0.2
Modulus at 300% elongation, MPa	3.8	0.8	0.2	0.6	0.2	0.4	0.4	0.4
Crystallization rate	very fast	med. to fast	medium	slow to med.	fast	very slow	slow	does not crystallize
Main features	high chlorine content and fast crystallization	high tensile strength	good tack and extensibility	good balance of tack and hot strength	best open tack time and good adhesion	excellent extensibility	low cost, fast curing	mechanical, electrolytic stability, and carboxyl functionality

### Anionic Types

Latex 400 contains a fast-crystallizing polymer which yields the highest uncured strength of all the Neoprene latexes, but the shortest dry open tack time. Successful use requires that substrates either be bonded wet, heat reactivated or bonded under high pressure. Adhesives based on Latex 400 have good resistance to weather, water, heat, and ozone. The polymer in Latex 400 also possesses the highest chlorine content of the Neoprene latexes and is often used in applications which require good resistance to degradation by flame.

Latex 571 contains a very high gel polymer which offers high strength films with low permanent set. Latex 571 is primarily used in combination with other latexes and resorcinol-formaldehyde resins for bonding elastomers to fibers and fabrics.

Latex 654 is a high solids, low viscosity latex containing a very low gel polymer which offers good tack and flexibility. It is generally used in wet laminating applications, for example, to adhere various facing materials to a variety of fiberglass batts and boards.

Latex 671A is a high solids, low viscosity latex containing a medium-high gel polymer which offers high uncured cohesive strength combined with good open tack time. It is used in both contact bond and wet laminating applications. It offers better hot strength than Latex 654 with a sacrifice in contactability.

Latex 750 contains medium gel, slow crystallizing polymer which gives an excellent combination of flexibility, dry tack, heat-reactivity and cohesive strength. It is used primarily in contact bond adhesives.

Latex 735A contains a sol polymer which gives the longest dry open tack time of all the latexes. Its films are also the most readily heat reactivated. Latex 735A is generally used in adhesives for wet laminating.

Latex 842A contains a very high gel polymer which crystallizes more slowly than the polymer in Latex 571. It is used primarily in foil laminating applications.

### Nonionic Type

Latex 115 contains a copolymer of chloroprene and methacrylic acid, stabilized with polyvinyl

alcohol. For many adhesive applications, Latex 115 offers two major advantages over the other Neoprene latexes:

1. Excellent colloidal stability.
2. Carboxyl functionality.

The excellent colloidal stability of Latex 115 gives it exceptional resistance to shear and a broad tolerance to a variety of materials that would destabilize the anionic Neoprene latexes.

The carboxyl functionality of Latex 115 gives it much better specific adhesion to a variety of nonporous substrates. In addition, it offers a means of room temperature cure through crosslinking with metal oxides. Zinc oxide is generally used at two to five parts, although other metal oxides are effective. Crosslinking can also be achieved with organic crosslinking agents such as methylol ureas, methylol melamines, and epoxies.

Latex 115 is used primarily in industrial contact bond applications. Formulations based on Latex 115, such as the one shown in Table 17, come the closest to matching the performance of Neoprene solvent-based contact cements.

Neoprene Latex 115 reacts slowly with zinc oxide in adhesive form, causing a gradual increase in the adhesive gel content. In contact bonding, where gel content directly affects the contactability of dry films, it is suggested that adhesives be used within six months.

### Compounding

**Antioxidants.** The presence of a good antioxidant in Neoprene compounds is essential for adequate protection against oxidation. Hindered *bis*-phenols, such as Wingstay L or Antioxidant 2246, are usually used where minimum discoloration and/or minimum staining is desired. Where discoloration is unimportant, amine type antioxidants are used.

**Metal Oxides.** Zinc oxide is the most effective metal oxide. French-process-type zinc oxide, which is low in lead content, is incorporated into the latex as a dispersion. Zinc oxide serves three main functions: (1) promotes cure; (2) improves aging, heat, and



weather resistance; and (3) serves as an acid acceptor.

For most adhesive applications, 2 phr of antioxidant, and from 2 to 5 phr of zinc oxide are adequate to provide the desired performance. In some more demanding applications, it may be beneficial to increase the amount of antioxidant and/or zinc oxide. Accelerated aging tests, simulating as close as possible the anticipated exposure the adhesive will encounter, should be conducted to be sure the amounts and types of ingredients added to the Neoprene will yield the performance required.

**Resins.** Because of colloidal incompatibility, the metal oxide/*t*-butyl phenolic resin complex which in solvent adhesives provides improved adhesion largely and hot strength is ineffective in latex systems. Of the types of resins which are commonly used in Neoprene latex adhesives, only the *terpene phenolics* such as Durez 12603 (Occidental) and SP-560 (Schenectady) do not cause an appreciable loss in hot strength as the resin content is increased. Others such as coumarone indene resins, liquid terpene resins and rosin esters are valuable from a standpoint of increasing adhesion and open time, but decrease cohesive strength at elevated temperatures. This is illustrated in Fig. 8, where canvas-to-canvas peel strength at 70°C (158°F) is plotted against resin level with several different classes of resins in Neoprene Latex 750. Only the terpene phenolic systems provided adhesive failure, even at the 50 phr

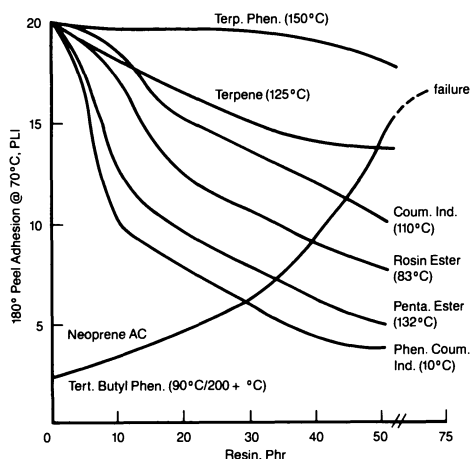


Fig. 8. Effect of resin type in neoprene Latex 750 adhesives. Bonds aged 7 days at R.T.

level. However, terpene phenolic resins are less tacky than many of the softer synthetic resins. They are frequently used in blends with other resins to achieve a better balance of hot strength and open time.

Resins are incorporated in Neoprene latex as solvent-cut emulsions, solventless pebble-milled dispersions, or sometimes as solvent-free emulsions prepared using *invert emulsification* techniques. In the latter case a resin with a melting point of 80°C (176°F) or lower is melted. Water and surfactants are added to the molten resin and the temperature of the mixture is decreased. Upon reaching a certain temperature, known as the phase inversion temperature, the water in molten resin emulsion spontaneously inverts to form a resin in water emulsion suitable for use in latex adhesives. A resin dispersion which can be prepared in this manner is shown in Table 16. This particular resin dispersion can be used to produce adhesives with moderate hot strength and good open time using the following recipe:

	% Solids	Dry Parts
Neoprene latex 671A	60	100
Antioxidant	33	2
Zinc oxide	50	5
Resin dispersion	50	30

Table 16. Resin Dispersion Made from Invert Emulsification Process.

Resin Suspension	Parts
Arizona Zonester 65 Resin <sup>a</sup>	100
Witcomul 4089 <sup>b</sup>	3
Igepal CO-970 <sup>c</sup>	3
Deionized water	94

**Procedure:**

1. Melt the resin and emulsifiers in a 100°C (212°F) circulating air oven.
2. Add resin mixture to temperature controlled vessel 85–90°C (185–194°F), and stir until mixture cools to 90–95°C (194–203°F).
3. Add 6 g of 85°C (185°F) water.
4. Cool mixture to 85°C (185°F). Slowly add 6 g of 85°C (185°F) water. Mixture will become thick as it inverts.
5. Add remaining water with thorough mixing. Cool to room temperature without stirring. Particle size should be 1–3 μm.

<sup>a</sup>Rosin ester, Arizona Chemical Corp.

<sup>b</sup>Rosin diethanol amide, Witco Chemical Corp.

<sup>c</sup>Ethoxylated nonyl phenol, GAF Corporation.

The solvent-free systems offer several advantages over emulsions which utilize solvent to dissolve the resin:

1. Ability to produce lower viscosity adhesives, as one avoids the thickening action of the solvent;
2. Higher resin content;
3. Addition of flammable solvents is averted; and
4. Greater latitude in controlling rheology with synthetic thickeners is gained by omission or reduction of the amounts of solvent, soap, and casein usually present in the emulsions.

**Fillers.** The Neoprene latexes are not significantly reinforced by the addition of fillers. Fillers are used to reduce cost and control rheology, solids content, and modulus. Both tend to reduce cohesion and adhesion. Hydrated alumina is often used when resistance to degradation by flame is important. In other cases, calcium carbonate, clay, silica, and feldspar are commonly used.

### Typical Formulations

Typical adhesives based on Neoprene latex are presented in Table 17. The first is a general-purpose contact adhesive. Either Latex 671A

or Latex 750 provide a good starting point in this formulation. The latter provides better contactability at the expense of hot cohesive strength.

The second formulation is a contact bond adhesive based on Neoprene Latex 115. It provides good cohesive strength development because of the reactivity of Latex 115. For best results, it should be used within six months after formulation.

The third and fourth formulations are designed for high-speed lamination of aluminum foil to kraft and other papers. Neoprene Latex 654 is a suitable choice in the anionic recipe because it can tolerate high filler loadings while retaining adequate "wet grab" performance. Neoprene Latex 115 is also a good choice for this application because of its excellent shear stability and adhesion. The fourth formulation provides a suitable starting point for evaluation.

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**Table 17. Neoprene Latex Starting-Point Adhesive Formulations.**

Ingredient	Dry Parts			
	Contact Bond	Contact Bond <sup>a</sup>	Foil to Paper Laminating	Foil to Paper Laminating <sup>b</sup>
Anionic Neoprene latex polymer	100	—	100	—
Neoprene Latex 115	—	100	—	100
Antifoam as required	—	—	X	X
Surfactants as required	X	X	X	X
Zinc oxide	5	2	5	5
Antioxidant	2	2	2	2
Terpene phenolic resin	50	—	—	—
Liquid polyterpene resin (low melting point)	25	—	—	—
Hydrogenated wood rosin or rosin ester	—	30	20	—
Filler	—	—	100	100
Resimene 717 <sup>c</sup>	—	—	—	5
Ammonium chloride	—	—	—	0.2
Thickener as required	X	X	X	X

<sup>a</sup>Adhesive should be used within 6 months.

<sup>b</sup>Ref. 15.

<sup>c</sup>Melamine formaldehyde resin, Monsanto.

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# Polysulfide Sealants and Adhesives

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The term *polysulfide polymers* referred at one time exclusively to the high-sulfur-containing polymers as manufactured by the Thiokol Chemical Corp. From 1928 to 1960 they were the only high-sulfur polymers available. The solid polysulfide polymers contained 37–82% bound sulfur, while the liquid polymers contain approximately 37%, which gives them their unique chemical properties.

Between 1960 and 1976 several new mercaptan terminated polymers having varied polymer backbones were introduced. These are covered in the section entitled “Other Mercaptan Terminated Polymers.” The chemical resistance of these various polymers can vary depending upon their backbone structure and, on this basis, should be evaluated on their own relative merits.

## POLYSULFIDE SEALANTS

Sealants based on polysulfide liquid polymers originally found wide acceptance for applications requiring a flexible, adhering, chemically resistant composition of matter. Since they were the first liquid polymers available that could be cured at room temperature, they were soon specified for a number of military applications. Their use as aircraft sealants for fuel tanks still remains as a major outlet. Other military applications included a quick hose repair compound, a sealant for bolted steel tanks for quick assembly on the battle front, electrical

potting compounds, caulks for wooden flight decks which were designed as a stop gap in the early days of aircraft carriers, sealing and adhering methacrylate bubbles on aircraft, sealing cocoons in the mothball fleets, adhering aluminum strips on wings for reducing air turbulence during flight, and many others. Most of these were emergency measures adopted for immediate use during the early 1940s and covered by quick-issue military specifications.

Use of polysulfides is at present largely restricted to sealants and insulating glass. Where these polymers were dominant in the 1960s and early 1970s, they are now a poor third as building sealants, giving way to silicones and urethanes. The decline of polysulfide sealants in the U.S. has been due in part to a price war which resulted in inferior-quality building sealants, causing many suppliers to switch to urethane. Some companies made their own urethane-base polymers while others bought a prepolymer from several sources. Another reason for the decline was the better performance available with urethane and silicone sealants. In Europe, the polysulfide sealants have a better market because of more rigid control of performance, application, and specification.

One continuing large application for polysulfide sealants is as a glass adhesive for making insulating glass units. This application started out in a small way in the early 1940s using a plasticized solid polysulfide polymer; but this was quickly replaced by the more versatile liq-

uid polymer. In recent years, polysulfide sealant, while still first, has been steadily giving ground to other systems including butyl hot melt and the dual system of silicone/polyisobutylene. The hot melts are cheaper, and lend themselves to automation and lower labor costs. The polysulfide systems are ending up as lower quality units for public housing and the home repair market which are not greatly affected or controlled by specifications. The high quality market for industrial and high rise buildings is now using some polysulfide, but the best units are made using a dual system of silicone/polyisobutylene. The trend will continue, with polysulfide losing out where high quality and good performance specification will prevail.

Another large market in the past was the use of polysulfide sealant as a glass adhesive for installing automotive windshields. In the original process, the glass was attached by metal trim on the assembly line. General Motors designed a three-part mixer which was made by Pyles Industries, and the use of the very fast-curing polysulfide actually lowered total costs. Thus polysulfide was adopted by General Motors for many of their models; later, Chrysler joined. This market lasted for approximately five years; but eventually the polysulfide was replaced by a simpler system consisting of a one-part urethane activated by mixing water into the sealant just before use. Here again, cost savings dictated the final selection.

The replacement market started out using a two-part polysulfide which was difficult to handle. This was quickly replaced by the one-part silicone, which was more expensive but more foolproof. In the replacement market, labor costs were less important.

Another large market which held sway for approximately 6 years in the early 1960s was the use of the sealant for military runway expansion joints. These sealants were highly extended with filler and coal tar, and used specialty polymers to meet the required low cost. The bubble burst when the sealants hardened with time, lost adhesion, and had to be replaced. The new system was a hot melt of plasticized PVC, which has done an admirable job with a simpler system and was eventually covered by ASTM specifications.

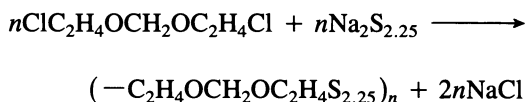
Areas where the polysulfide sealants are still used include dental impression compounds, cast printing rolls, casting compounds for flexible molds, electrical potting, and miscellaneous adhesives.

Polysulfide sealants are excellent adhesives and adhere to a wide variety of surfaces; but price inevitably plays a major role in the final selection of material used for high-volume applications.

## Chemistry

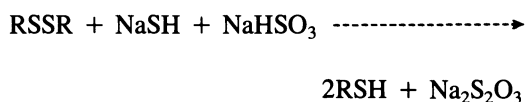
Many of the sealants have been prepared using Thiokol® LP®-2, LP®-32 or LP®-31 as the base polysulfide liquid polymer; the chemistry, cure mechanisms, reinforcement, and applications will thus be restricted to these polymers. The chemistry and applications of polysulfide polymers, crudes, water dispersions, and various liquid polymers are covered completely in extensive bibliographies by Berenbaum and Pank. <sup>21</sup>

The general preparation of polysulfide liquid polymers, as discussed by Patrick and Ferguson <sup>22</sup> involves first the reaction of bis-chloroethyl formal with a sodium polysulfide solution containing specific emulsifying and nucleating agents as shown below:



The sulfur is present as a mixture of disulfide and trisulfide.

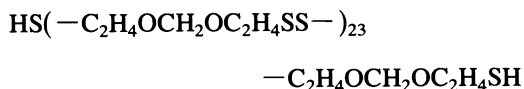
In the next step, the high molecular weight polymer is split into segments which are simultaneously terminated by mercaptan groups as shown below:



The concentration of splitting salts controls the average molecular weight of the LP®2 and

®Registered trademark of Thiokol Chemical Corp.

LP®32, which have the following average formula:



Both polymers are prepared at an average molecular weight of 4000, and they differ only in the mole percentage of crosslinking agent (trichloropropane) used in the initial reaction. LP-2 is made using 2 mole % of trichloropropane, whereas LP-32 is prepared with 0.5%.

Decreasing the crosslinking agent gives lower modulus and higher elongation desirable in applications involving greater movement. In some instances LP-31 is used in sealant applications; it differs from LP-32 in that it has a higher molecular weight and viscosity. The physical properties of the three polymers used in sealant applications are compared in Table 1.

### Compounding

Polysulfide sealants are formulated using reinforcing fillers, plasticizers, adhesive additives, and curing agents. Table 2 illustrates five types of compounds for use in several industries:

1. One-part sealants, which generally use a lower polymer content for better package stability.

2. Building sealants. In practice, polymer ratios have been observed to be lower.
3. Insulating glass sealants; the lower plasticizer content and higher filler content give the higher hardness which is needed for this application.
4. Aircraft sealants, where plasticizer content is kept at a minimum to reduce extraction by jet fuels.
5. General purpose casting compound with high plasticizer and good flow properties.

The various groups of compounding ingredients are discussed separately.

### Curing Agents

While a large number of curing agents have been tried, only a few have been found satisfactory. A technical grade of lead dioxide is used for most two-part building sealants and casting compounds. Stearic acid is used as a retarder which is incorporated in the curing agent paste. The paste is usually 50% lead dioxide, 45% plasticizer, and 5% stearic acid.

A technical grade of manganese dioxide is used as a curing agent for insulating glass sealants since the cured compounds have better UV resistance through glass and retain adhesion for extended periods of time. A base serves to accelerate the manganese dioxide to give about

**Table 1. The Physical Properties of LP® Polysulfide Liquid Polymers.**

	<i>LP-31</i>	<i>LP-2</i>	<i>LP-32</i>
Viscosity at 25°F (poises)	800–1400	375–425	375–425
Average molecular weight	8000	4000	4000
Specific gravity	1.29	1.29	1.29
Refractive index	1.5728	1.5689	1.5689
Pour point (°F)	50	45	45
Flash point, (open cup)°F	455	450	455
Fire point, (open cup)°F	475	475	485
Crosslinking agent (%)	0.5	2.0	0.5

**Table 2. Good Formulations for Several Applications, by Weight**

	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>
polysulfide polymer	20	35	30	65	35
fillers	50	40	50	25	35
plasticizers	25	20	15	5	27
adhesion additive	2	2	2	2	—
curing agents	3	3	3	3	3

30 minutes of work life and a cure in approximately 8 hours. The compounds are adjusted to work with proper equipment.

One-part sealants use calcium peroxide as a curing agent since it is inert in an anhydrous environment. In this sealant, barium oxide is incorporated as a dehydrating agent which is added last, but just before the addition of the calcium peroxide paste. The barium peroxide picks up 6 molecules of water of hydration and is very effective in making the sealant package stable.

Other curing agents have included inorganic chromates in aircraft sealants requiring better heat resistance. Some manganese has also been used for aircraft sealants. Cumene hydroperoxide has found a place in a few casting compounds; but in building sealants, it interferes with adhesion.

### Fillers

Some reinforcement is required for polysulfide sealants. For aircraft compounds, some carbon black is needed for higher physicals. For all other applications the chief fillers are the calcium carbonates, which are available as ground marble dust or a precipitated grade. The cheapest sealants use mostly marble dust, but some precipitated grade is needed for thixotropy control.

For insulating glass sealants, some titanium dioxide serves to make the base white, while a small amount of carbon black is added to the catalyst. Since the components are mixed by pumping metered amounts of both components through a patented static tube, any streaking will indicate incomplete mixing. A thorough mix gives a uniform light gray color. Some calcined clay has been used in building sealants to neutralize the alkalinity from the carbonates. Lithopone and zinc sulfide have been used in place of titanium dioxide.

### Plasticizers

At one time the chlorinated diphenyls were widely used in polysulfide sealants; but because of their toxicity they were replaced by phthalate, phosphate, and glycolate esters. Some toluol solvent is used to improve the ex-

trusion properties; but it is kept at a minimum. Insulating glass sealants would require less volatile plasticizers in order to eliminate any fogging within the unit.

### Adhesion

Where adhesion is required, all sealants need an adhesion additive. For two-part building sealants, a selected phenolic resin (Methylon AP-108, General Electric) has been very satisfactory. A silane monomer is used for the one-part sealants. Aircraft sealants have used a selected phenolic resin which is more resistant to the jet fuels. A Durez resin, #10694 (Occidental Chemical Corporation) has been most satisfactory.

### Primers

All building sealants contain adhesion additives, but many times this is not enough. For bare metals, a dilute silane based primer is recommended. For porous surfaces, a film-forming primer is needed to seal off any water that might migrate to the interface. Primers have also been used to seal off any gases that might permeate through the substrate. For unusual building surfaces, all sealant manufacturers have additional primers in their bags of tricks. The masonry primers generally contain a chlorinated rubber or a modified phenolic resin or both, along with some plasticizer. The primer is very specific for the sealant, and is supplied by the sealant manufacturer. The low-solids silane primers provide monomolecular films which result in adhesion to metals, glass, and ceramics.

### Specifications

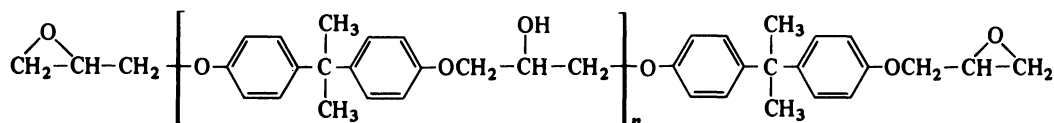
Specifications for building sealants include the Federal specifications TT-S-00227E for multi-part and TT-S-00230C for one-part, as well as ASTM C-920 for both parts. This specification has been selected in 1972 by the National Bureau of Standards to replace the Federal specifications. Other military specifications which are still being used are:

1. MIL-S-7502C—aircraft fuel tank sealing.
2. MIL-S-8802C—high temperature resistant fuel tank sealing.

3. MIL-S-8516C—electrical potting.
4. MIL-C-15705A—seam sealer for aircraft.

### ADHESIVES FROM POLYSULFIDE LIQUID POLYMER-EPOXY RESIN REACTIONS

The first reactions of polysulfide liquid polymers with epoxy resins were studied by Fettes

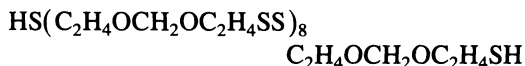


and Gannon.<sup>23</sup> It immediately became apparent that the reaction between these two classes of polymeric compounds gave reaction products which could be considered in compositions for applications involving castings, coatings, laminates, potting, adhesives, etc. The complete treatment of this extremely versatile class of reaction compounds is given by Berenbaum and Panek.<sup>21</sup>

This discussion will be limited to adhesive compounds. In formulations developed for adhesives, the epoxy resin is the major component. However, modification of the epoxy resin with polysulfide liquid polymers gives compositions which in many cases have unique physical and chemical properties.

#### Chemistry

Of the several polysulfide liquid polymers which have been studied, LP-3 has been used most extensively. The average formula for this polymer is:



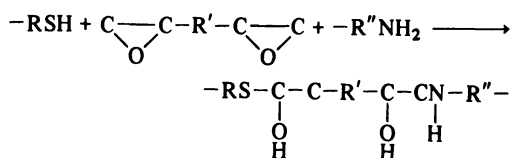
This polymer has an average molecular weight of 1000 and a viscosity of 7 to 12 poises. It is prepared using 2 mole % of trichloropropane, which gives a measurable amount of crosslinking when cured alone; this, however, is not readily apparent when cured with epoxy resins.

A number of liquid epoxy resins as well as blends of liquid and solid epoxy resins have

been studied. The most widely used resins are found in the viscosity range of 80 to 200 poises and have an epoxy equivalent of 175 to 210. Examples of epoxy resins within this classification are Epon\* 820 and Epon\* 828 (Shell Chemical Co.), ERL-3794 (Union Carbide), and Araldite\* 6020 (Ciba Co.,).

The epoxy resins, which are reaction products of bisphenol A and epichlorohydrin, have the following idealized formula:

This reaction between polysulfide liquid polymers and epoxy resins is catalyzed or promoted by organic amine compounds. Although a considerable number have been evaluated, final selection has narrowed the list down to a few practical catalysts among which are: DMP-30®, Rohm and Haas) (tri-dimethylamino-methyl phenol), DET (diethylenetriamine), and BDA (benzyl dimethylamine). The amine catalysts are used in a fairly high ratio, in most cases 10% based on weight of the epoxy resin. Because of the coreaction of primary amines such as DET, they are more properly classified as reactive hardeners. The general reaction of a polysulfide liquid polymer, an epoxy resin, and a primary amine hardener is:



#### Physical Properties

LP®-3 polymer, when used to modify a liquid epoxy resin cured with DMP-30, accelerates the cure and increases the maximum temperature due to reaction exotherm. The use of LP-3 with epoxy resins gives compositions which have higher elongation, greater impact resistance, and less brittleness. The effect of increasing amounts of LP-3 on the physical

\*Registered trademark, U.S. Patent Office.



properties of a liquid polymer epoxy resin is given in Table 3.

It is interesting to note the increase in tensile properties of the epoxy resin by adding up to 50% LP-3. The straight epoxy-resin cured compound theoretically has higher tensile, but due to its low elongation, breaks before its ultimate tensile may be realized. The combination of increased flexibility, tensile strength, and elongation is very desirable in adhesives.

The improved impact resistance of compositions containing LP-3 is apparent as well as very desirable in certain adhesive formulations.

The heat distortion temperature is only slightly affected by the incorporation of 20% LP-3, but at 1:1 ratio the drop may become significant. This is illustrated by the fact that a straight epoxy resin cured with DET has a heat distortion temperature of 55°C which is reduced to 54°C when the LP®3/epoxy resin ratio is 1:4, to 50°C at a 1:2 ratio; and to 40°C at a 1:1 ratio. These specific properties prevent the use of such compositions at elevated temperature adhesives but do not deter their use when proper temperature limitations are maintained.

The electrical properties of LP-3 epoxy resin compounds are only slightly lower than those of unmodified epoxies, even when a 1:1 ratio is used. These compounds thus can be used in electrical potting.

The adhesive properties of LP-3/epoxy compounds are better than those of the epoxy alone, as is illustrated in Table 4.

The data compare compositions after an oven cure of 1 hr at 250°F, which is considered optimum. Shear bond strengths of LP-3-modified compositions are appreciably higher than straight epoxy compositions in various environments involving changes in temperature or immersion media.

Similar improvement is obtained in peel and bend strengths, a result of improved flexural properties through the use of LP-3.

### Applications

One very practical application for the LP-3 epoxy adhesives is in bonding old-to-old concrete and new-to-old concrete. These adhesives have definite applications in the construction and maintenance of concrete structures such as highways, bridges, buildings, dams, airport runways, sidewalks, driveways, commercial and industrial floors for patching, overlaying, surface sealing, and skid proofing, as well as a number of other operations. Table 5 illustrates the improved adhesive properties obtained using an LP/EP concrete adhesive as compared to a straight epoxy resin compound. The LP/EP compounds show considerably improved bond strengths that, in almost all cases are limited only by the strengths of the concrete. These compositions are unique in applications involving adhering new freshly poured concrete to old concrete. Bonds based on these assemblies exhibit the same adhesive values.

**Table 3. The Effect of LP®3 Polymer on the Physical Properties of Liquid Epoxy Resin.**

Epoxy resin <sup>a</sup>	100	100	100	100	100	100	100
LP-3	—	25	33	50	75	100	200
DMP-30	10	10	10	10	10	10	10
Physical Properties on Sheets Cured for 7 days at 77°F.							
Tensile (psi)	3500	5500	6500	7200	3075	2350	150
Elongation (%)	0	1	2	5	7	10	300
Shore D Hardness	80	80	80	80	76	76	15
Coefficient of linear expansion (in./in./°C × 10 <sup>5</sup> )	4.5	5.5	6.0	7.5	10.0	13.5	15.0
Impact resistance (ft-lb)	2	1	3	5	27	70	100

<sup>a</sup> Liquid epoxy resin, epoxy equivalent 175 to 210.

\* Registered trademark U.S. Patent Office.

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**Table 4. Comparison of Adhesive Values on Aluminum.**

	Straight Epoxy Control		LP/EP Adhesive	
	A	B	A	B
Thiokol® LP-3	—	—	100	—
Liquid epoxy resin <sup>a</sup>	—	100	—	100
Calcium carbonate	—	100	71	179
EH-330	15	—	15	—
A/B ratio	1/13.3		1/1.5	
Cure (considered optimum)	1 hr at 250° F		1 hr at 250° F	
Tensile shear bond strengths psi tested at 0.05 in./min				
Tested at room temperature	1700		4500	
Tested at 180° F	2000		1500	
Tested at -67° F	1400		2500	
Peel Strength lb/in.	8		18	
Bend Bond Strengths lb	100		140	
Shear Bond Strengths after 30 Days Drop Immersion in Various Media at 80° F.				
Water	1000		1700	
Seawater	0		1100	
JP-4 fuel	1800		3200	
Isopropyl alcohol	2000		3200	
Ethylene glycol	1600		3700	
Engine oil	1700		3200	
Methyl ethyl ketone	1600		500	
Dibutylphthalate	1800		3400	

<sup>a</sup> Liquid epoxy resin epoxide equivalent 175 to 210.

## OTHER MERCAPTAN-TERMINATED POLYMERS

In recent years three classes of mercaptan-terminated polymers have been introduced to industry. In the 1960s Diamond Alkali offered several polymers having a polyether backbone terminated with mercaptan groups.<sup>1,2</sup> These polymers were cured in the same manner as the Thiokol polysulfide polymers, but were withdrawn after several years, since their properties were generally poorer and offered no advantages. Products Research came out with polymers having a urethane backbone but with mercaptan terminals; however, they sold only finished sealants, mainly for the insulating glass industry. These polymers are still being manufactured by PRC.<sup>4,19,20</sup> In the early 1970s

**Table 5. Comparison of Concrete Adhesive Values.**

	Straight Epoxy Control		LP/EP Concrete Adhesive	
	A	B	A	B
Thiokol® LP-3	—	—	100	—
Silica Filler	—	50	80	—
DMP-30	7.5	—	20	—
Liquid epoxy resin <sup>a</sup>	—	100	—	200
A/B ratio	1/120		1/1	

### Tensile Adhesion Values, psi

Tested at room temperature and after 7 days cure 0-150 345

Tested at room temperature and after 7 days water immersion 0-150 335

### Verticle Bond-Flexural Strength lb/sq in

Tested at room temperature and after 7 days cure 35 335

*Note:* Values are practically identical whether bonding old-to-old concrete or new-to-old concrete. Concrete was prepared using ASTM Designation C-185. Tensile adhesion assemblies and tests complied with ASTM Designation C-190, whereas flexural assemblies and tests complied with ASTM Designation C-348.

### Comparison of Shear Strength at Various Temperatures (psi)

	Straight Epoxy Control	LP/EP Concrete Adhesive
Tested at room temperature and after 7 days cure at:		
(°F)		
150	400	4200
212	300	4300
350	100	100

<sup>a</sup>Liquid epoxy resin, epoxide equivalent 175-210.

Hooker Chemical introduced pilot plant batches of still another commercial venture. These polymers had a polyethylene backbone and mercaptan terminals, but the polymer had a very high sulfur content of 55%. The venture was dropped when again the polymers had poorer properties than the Thiokol polysulfide poly-

mers. The References cite a number of patents covering various mercaptan-terminated polymers of academic interest. In the summary below, the literature is grouped into similar polymeric backbone structures wherever possible.

### Polyethers

Several patents are cited which involve a polyether backbone. LeFave and Hayashi prepared polymers having a poly (oxyalkylene) polyol backbone terminated with mercaptan groups by esterifying the polyol with thio-substituted organic acids. These polymers were cured with tetramethy-thiuramdisulfide and  $\text{MnO}_2$ . LeFave and others<sup>2</sup> also prepared similar polymers by reacting the polyols with an epihalohydrin and then reacting the intermediate with sodium sulfhydrylate. These polymers are cured with  $\text{PbO}_2$ ,  $\text{MnO}_2$ ,  $\text{ZnO}_2$  and  $\text{TiO}_2$  to give rubbery products.

Ephraim<sup>3</sup> prepared thiol-terminated polyethers by polymerizing a halogen-containing epoxide alone or in combination with an alkylene oxide and then converting the halo groups to thiol groups using an alkali hydrosulfide.

Morris and others<sup>4</sup> reacted a poly (oxyalkylene) glycol with an alkali metal in dispersion, and treated the alcoholate with a halogenated organic compound, and then reacting further with a sulfur containing compound and, finally, hydrolyzing with an alkali metal to yield the mercaptan terminated polyether.

Nummy<sup>5</sup> prepared intermediates by reacting the divinyl ether of diethylene glycol with  $\text{H}_2\text{S}$  to yield the bis(2-mercaptoethyl) ether of diethylene glycol, then oxidized this monomer to give a range of mercaptan-terminated liquid polyether polymers.

### Polyesters

Erickson<sup>6</sup> reacted diacrylate-terminated esters with  $\text{H}_2\text{S}$  to obtain mercaptan-terminated polymers. These polymers can be cured using dicumyl peroxide and  $\text{MgO}$  to give rubbery compounds. Cameron and Duke<sup>7</sup> disclosed mercaptan-terminated polyesters made by reacting glycols with mercapto-organic acids.

These polymers are cured using  $\text{PbO}_2$  and other oxidizing agents.

### Urethanes

Bertozi<sup>8</sup> synthesized a class of polythiopolymercaptan-polyurethane polymers by reacting disulfide—containing polyols, diisocyanates, and dimercaptans. These polymers were readily cured with oxidizing agents. Gobran<sup>9</sup> caps urethane prepolymers with nonpolymeric polymercaptans to yield mercaptan terminated ureas, thio-urethane linked polyesters, or polyether polyurethanes. Bertozi<sup>10</sup> reacted mercaptoalcohols with organic polyisocyanates to yield mercaptan-containing polyurethane compositions which were easily cured with  $\text{PbO}_2$  and  $\text{Li}_2\text{O}_2$ .<sup>19</sup> Smith<sup>11</sup> prepared mercaptan-terminated urethane-linked polyethers by reacting a polyether glycol with an epihalohydrin, then reacting with a polyisocyanate. This polymer was then treated with an alkali metal sulfhydrylate to remove the chlorine terminals and yield the desired polymers.

### Olefin

Noll and McCarthy<sup>12</sup> prepared branched chain mercaptan-terminated polybutadiene by polymerizing the polybutadiene with a xanthogen disulfide and pyrolyzing the ester. Weinstein and others<sup>13</sup> reacted a conjugated diene with sulfur which is then hydrogenated to produce polymers of low molecular weight containing mercaptan groups. Warner<sup>14</sup> and Franz<sup>15</sup> reacted conjugated dienes with  $\text{H}_2\text{S}$  to yield mercaptan derivatives of polybutadiene, alone or in combination with other coreactants.

### Miscellaneous

Jones<sup>16</sup> prepared polyether-polyester polymercaptans by reacting polyols with mercaptoorganic acids and oxidized the resulting prepolymers to give higher molecular weight polymercaptans which were easily cured with  $\text{PbO}_2$ . Warner<sup>17</sup> irradiated mixtures of ethylcyclohexyl-dimercaptan and vinyl cyclohexene to yield thiol-terminated polymers.

Bertozi<sup>18</sup> prepared polymercaptan polymers by reacting polymers containing geminal di-

thioether linkages with water in the presence of a strong nonoxidizing acid.

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# Phenolic Resin Adhesives

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Phenolic resins have played an important role in industrial advancement for over 80 years. The term *phenolic* is applied to those materials formed during the condensation reaction between phenol or substituted phenols and formaldehyde. Although Adolph Baeyer<sup>1</sup> first reacted phenol and an aldehyde in 1872 to produce a resinous material, and Arthur Smith was issued the first phenolic resin patent in 1899,<sup>2</sup> it is Leo H. Baekeland who is considered the creator of the phenolic resin industry. He published a series of papers<sup>3,4</sup> beginning in 1905, and established the Bakelite Company in the U.S. in 1910. This eventually became a division of the Union Carbide Company in 1939.<sup>2</sup> Over the years many scientists have helped make phenolic resin products an integral part of modern life.

The basic production data<sup>5</sup> shown in Table 1 illustrate the large quantity of phenolic resins used in United States markets from 1983 to 1987 as well as the important product lines. The total resin output has grown from 2.54 to 2.76 billion lb during those five years. However, from examining the table it is apparent that plywood adhesives and related housing markets consume the largest quantity of resin and continue growing, but that product lines such as abrasives, foundry, and molding resins have been decreasing. Some of these reversed trends are due to competition from other engineering

plastics as well as to economic factors. Since new phenolic composites show excellent thermal stability and flame retardant characteristics, considerable development and growth are expected in many specialty areas. Sections are included in this chapter on molding compounds and coatings to examine some of the special adhesive binding properties of phenolic resins when used in other than thin films.

Scientific activity continues to grow in both basic research and applications. It is interesting to look at the patents<sup>6</sup> issued by country during the years 1981–1987. The results in Table 2 show substantial commercial development in the phenolic field and also illustrate the large contribution from Japan to the patent literature. In 1982–1986 alone<sup>6</sup> there were 4620 articles, excluding patents, pertaining specifically to phenolic chemistry and technology.

## CHEMISTRY

Building upon the early work in phenolic resins which was summarized in several excellent books,<sup>7–10</sup> considerable advancement has been made in understanding the chemistry, molecular structure and application properties of phenolics. Much of this new insight parallels the enormous growth in instrumentation and new techniques such as superconducting Fourier Transform nuclear magnetic resonance

**Table 1. Phenolic Resins Consumption, millions of lb.<sup>5</sup>**

Market	1983 <sup>a</sup>	1984 <sup>a,b</sup>	1985	1986	1987
Bonding and adhesive resins for:					
Coated and bonded abrasives	29	26	16	17	18
Fibrous and granulated wood	179	183	217	235	226
Friction materials	33	37	26	27	29
Foundry and shell moldings	71	79	77	41	41
Insulation materials	355	353	419	420	421
Laminating:					
Building	40	37	32	40	48
Electrical/electronics	31	33	20	22	25
Furniture	20	20	20	22	25
Other	75	73	70	83	95
Plywood	1312	1323	1255	1270	1346
Molding compounds	231	245	209	195	197
Protective coatings	18	20	23	22	23
Export	22	26	21	18	20
Other	121	128	235	250	250
<b>TOTAL</b>	<b>2537</b>	<b>2583</b>	<b>2640</b>	<b>2662</b>	<b>2764</b>

<sup>a</sup>Converted from metric tons.<sup>b</sup>Some slightly different values were given in *Mod. Plast.*, 63, 62 (1986).**Table 2. 1981–1987 Patent Activity in Phenolics by Country.<sup>a</sup>**

Total Patents <sup>b</sup>	Years	USA	Canada	Japan	West Germany	France	Britain	Sweden	USSR
2,205	1980–81	162	14	1,199	211	50 <sup>c</sup>	56	105	279
6,688	1982–86	590	31	4,217	822	506	495	475	536
1,818	1987	110	5	1,287	248	157	155	72	53
10,711	1980–87	862	50	6,703	1,281	713	706	652	868

<sup>a</sup>Patents documented as given by the country. This includes some multiple single patent entries to countries from the EPO and WIPO.<sup>b</sup>The primary phenolics patents (single entry)—all countries.<sup>c</sup>Estimated value.

(FTNMR) and advanced chromatographic separations. Several recent treatises on phenolics are available.<sup>11–15</sup>

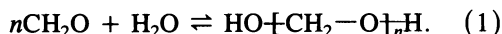
Phenolics which are formed when the molar ratio of formaldehyde to phenol is greater than one are called *resoles*. The phenol moieties are terminated with reactive hydroxymethyl groups ( $-\text{CH}_2\text{OH}$ ), known as methylol groups. If the mole ratio of formaldehyde to phenol is less than one, the polymer becomes phenol terminated and is called a *novolak*. All phenolic chemistry today revolves about these two basic chemistry strategies. Although phenol is most commonly involved in phenolics, resins containing *p*-*t*-butylphenol, *p*-*t*-amylphenol, *p*-nonylphenol, mixed cresols, and substituted

oils derived from cashew nutshell liquid are also used. Because the catalyst, mole ratio of phenol to formaldehyde, reaction conditions, addition sequence, and solvent conditions can be varied, an enormous variety of products can be tailored for specific end uses. When phenolic resins are involved in composites, the variety of properties becomes even richer. The majority of the syntheses rely on formaldehyde, so it is important to examine the nature of this structure in solution.

### Formaldehyde

The reaction mechanism for the formation of phenolic resins under acidic or basic catalysis

conditions depends on the molecular nature of the formaldehyde in the reaction medium. Formaldehyde is found in aqueous solution as a series of oligomeric poly(methylene) glycols,<sup>16,17</sup>



The most concentrated component in this complex equilibrium is methylene glycol<sup>16</sup> ( $n = 1$ ) with a formation equilibrium constant,  $K = 5 \times 10^2$  at  $60^\circ\text{C}$ . Studies on the  $^{13}\text{C}$  NMR spectra of the glycol oligomers<sup>18,19</sup> and the reaction mechanisms under acidic and basic conditions have been done.<sup>20</sup> In an acidic medium the unique formaldehyde molecule takes the form of a carbonium ion, whereas in a basic medium it reacts through an ionic species generated from the diglycol molecular form. It was shown in an early NMR study by Woodbrey<sup>21</sup> that if other hydroxyl groups are present, like on phenol or methanol, hemiacetals are formed. Raman and infrared spectra and other specific reactions are covered in Meyer<sup>16</sup> and Walker.<sup>17</sup>

### Novolaks

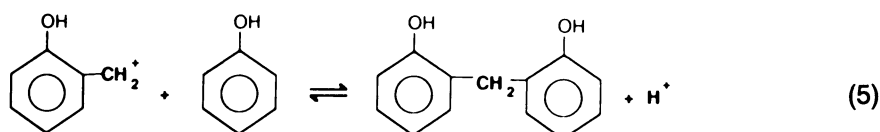
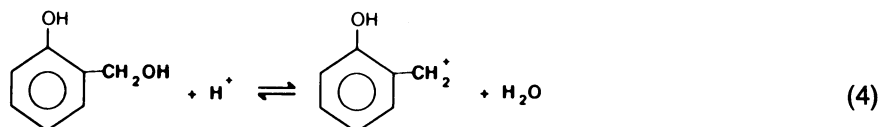
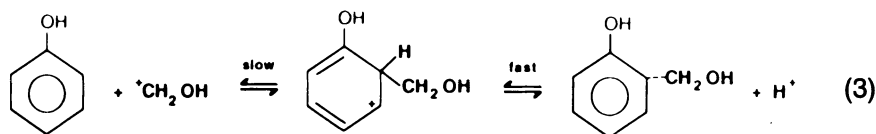
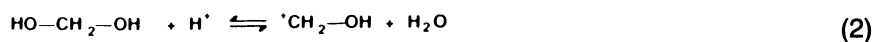
Resins that are made using acid catalysis and mole ratios of formaldehyde to phenol less than one are called novolaks. The word *novolak*

stems from an early trademark named by Baekeland<sup>22</sup> in 1909. This original shellac substitute became known in its generic form as *novolac*. In general, the novolak resins are called two-step resins, since in order to effect a cure another reactive component needs to be added to the system. This can be a resole, an aminophenol, or more commonly, hexamethylene-tetramine (HMTA).

Novolak materials do not contain active methylol groups as do resoles, and consequently are relatively stable to molecular weight advancement. They are amorphous thermoplastics that can be stored easily as powdered or flaked materials. According to Vansheidt, number average molecular weights varied in parabolic form from 200 at an F/P = 0.1 ratio to 1000 at a 0.8 ratio.<sup>23</sup> Others have found number average molecular weights of 950 by VPO at a mole ratio of 0.83<sup>24</sup> and 900 by GPC at a mole ratio of 0.80<sup>15</sup>. Molecular weights of fractionated F/P = 0.83 novolaks range from 200 to 8,000.<sup>25,26</sup> Glass transition temperatures  $T_g$  range from  $50^\circ\text{C}$  uncured<sup>27,28</sup> to  $287^\circ\text{C}$  when fully cured in composites.<sup>29</sup>

### Strong Acid Reactions

The reaction mechanism in a strong acid medium with  $\text{pH} < 4$  is shown in Eqs. (2)–(5).



The rearrangement to methylol phenol as shown in Eq. (3) is very fast in a strong acid medium. The methylol group is then converted to a carbonium ion which readily reacts with a neutral phenol molecule to form a dihydroxydiphenylmethane, Eq. (5).<sup>12</sup> Consequently, with mole ratios of formaldehyde to phenol less than one, no methylol groups are found in these structures.<sup>11</sup> The reaction kinetics for systems containing an excess of phenol are first order in formaldehyde and independent of the chemical nature of the formaldehyde when added. Acid catalysts employed in novolak syntheses include hydrochloric, sulfuric, oxalic, *p*-toluenesulfonic, and phosphoric acids. The *pH* in the synthesis is commonly in the range of 0.5–1.5 and the formaldehyde used is typically 37–50 wt% in aqueous solutions. There are three basic isomers formed in the reaction that depend on *pH*. The 2,4'- and 4,4'-dihydroxydiphenylmethanes are formed under strong acid conditions, whereas the 2,2'-dihydroxydiphenylmethane is favored in the 4–6 *pH* range.<sup>30</sup>

### Weak Acid Reactions

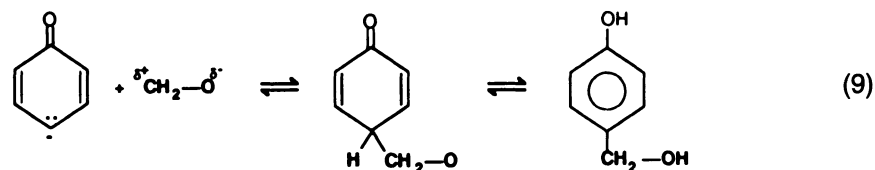
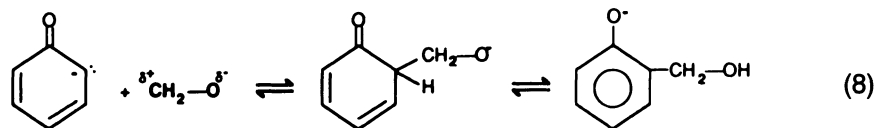
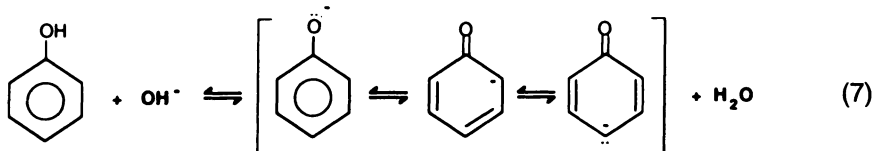
The weak acid area, *pH* 4–7, allows the preparation of the important high-*ortho* novolak resins. These resins can be prepared as solid novolaks or liquid resoles depending on the formaldehyde/phenol mole ratio. It has been recognized that having free *para* positions en-

hance the cure rate of these resins when compared to the mixed isomeric and branched resins. The high-*ortho* resins are generally prepared in aqueous solutions containing Ca, Mg, Zn, Cd, Co, Ni, Cu, or Pb divalent salts in a *pH* range of 4–6. One of the preferred catalysts is zinc acetate. The novolak processes make use of large molar excesses of phenol, with final postreaction temperatures at 150–160°C to promote condensation of the hydroxymethyl groups.<sup>11</sup> The reaction mechanism thought responsible for this pathway is the metal ion complexation in the *ortho* position of the *o*-methylolphenol.

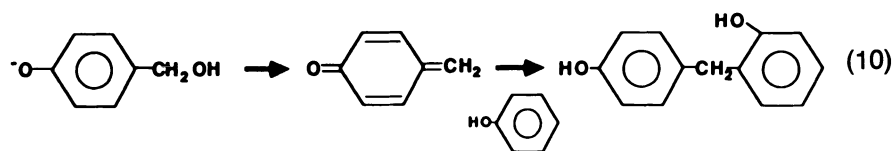
### Resoles

Resoles contain methylol end groups and are very dynamic resins, always advancing toward a cured state. The resole resin is a one-stage or one-step thermosetting resin. That is, it can be irreversibly cured with temperature and pressure. Many resoles are reacted in strongly basic media. The primary reaction pathway depends on both the nature of the formaldehyde and the phenol in a basic medium.

The reaction mechanism steps are depicted in Eq. (6)–(10). The formaldehyde reacts as a species generated from methylene glycol or oligomeric methylene glycol. The phenate ion is formed in a basic medium, and this hybrid of several resonance structures is an ideal nucleophile.







The reaction mechanism for the basic catalysis of phenolics is not completely understood. However, the reaction kinetics are known to be first order in methylene glycol and in phenol. A complete comparison of the relative reaction rates of producing the seven possible methylol phenols is given by Knop<sup>11</sup> and Pizzi.<sup>12</sup> Table 3 shows the rate constants,<sup>31</sup> the relative rate constants compared to 4-hydroxymethyl phenol (4-HMP) and the relative rate constants after allowing for the statistical weighting of the two *ortho* positions in both phenol and 4-hydroxymethylphenol. Comparison of kinetic rate constants for formaldehyde addition in the *ortho* positions relative to the kinetic rate constant for the addition of formaldehyde to phenol in the *para* position shows that the formation of 2-hydroxybenzyl alcohol is favored over 4-hydroxybenzyl alcohol 1.7:1. The formation of the 2,4-dihydroxymethylphenol (2,4-HMP) is 1.2:1 compared to the formation of 2,6-dihydroxymethylphenol at 1.40:1. Interestingly, the 2,4,6-trihydroxymethylphenol (2,4,6-HMP) forms at a ratio of 6.73:1 from the 2,6-dihydroxymethyl phenol, but only 1.5:1 from the 2,4-HMP relative to formation of 4-HMP. Since two pathways lead to 2,4-HMP, it still becomes an effective route for producing 2,4,6-HMP. These relative rates show the dynamics in resole resins toward forming trifunctional polyalcohols and consequently toward branching and gelling. It is also clear that 4-HMP,

2,4-HMP, and phenol would be left in a cook even as condensation advances. Several computer studies predicting the buildup of resin intermediates have been made.<sup>32,33</sup> Table 4 highlights some major differences between resoles and novolaks.

The variety of cooks and formulations using resoles is enormous. Consequently, it is important to understand that it makes a difference how the cook is formulated as to whether the resin is going into a wood bonding adhesive, a resole varnish, an impregnating resin, or a foundry resin application. Although many cooks are run with a formaldehyde-to-phenol mole ratio of 1.2–1.8, a wider range is possible. For example, if branching is desired, then an initial low temperature cook with a high F/P mole ratio will generate the largest concentration of trifunctional methylol monomers, especially if the initial cooking temperature is near 60°C or lower. This naturally leads to a three-dimensional crosslinked structure which implies solution instability in storage due to rapid viscosity buildup.

Resins that are primarily in the polymethylol noncondensed form are called *A-stage* resins and are easily soluble in water, alcohols and ketones. Further into the condensation, when dimers, trimers, and higher oligomers are formed, resins are labeled *B-stage*; and finally, when curing, they are called *C-stage* resins. Resoles are insoluble and intractable resins

**Table 3. Resole Kinetic Parameters for Formaldehyde Addition at 30°C.<sup>a</sup>**

Reaction <sup>b</sup>	$k \times 10^{-6}, l \text{ mol}^{-1} \text{ s}^{-1}$	Relative Formation <sup>c</sup>	Relative Rates <sup>d</sup>
Phenol-2-HMP	10.5	1.69	0.84
Phenol-4-HMP	6.2	1.00	1.00
2-HMP-2,6-HMP	8.7	1.40	1.40
2-HMP-2,4-HMP	7.3	1.18	1.18
4-HMP-2,4-HMP	7.5	1.21	0.60
2,4-HMP-2,4,6-HMP	9.1	1.47	1.47
2,2-HMP-2,4,6-HMP	41.7	6.73	6.73

<sup>a</sup>Freeman and Lewis ref. 31.

<sup>b</sup>Formaldehyde addition reactions.

<sup>c</sup>Values are relative to formation of 4-HMP.

<sup>d</sup>Reactions with phenol and 4-HMP have two *ortho* sites.

**Table 4. Summary of the Characteristics of Resole and Novolak Resins.**

Characteristic	Novolak	Resole
Mole ratio P/F	> 1	< 1
pH/catalyst	acidic	basic
Addition reaction	slow	fast
Condensation	fast	slow
Reaction rate	second order	second order
End groups	phenol	methylol
Chain structure	linear	branched
Molecular weight	200-8000	200-30,000
Molecular wt. dist.	narrower	broader

when cured. Number average molecular weights as high as 10,000 have been found in fractionated resole resins.<sup>34</sup>

A method of obtaining high ortho resole structures has been reported in a patent issued to Monsanto.<sup>35</sup> Toluene or xylene is used to form an azeotropic solvent with the high *ortho* content promoted by the continuous removal of the water by distillation. These materials have important applications as binders and molding resins.

### Dispersion Resoles

In many cases resoles are prepared as solutions since they are water or solvent soluble in the hydroxymethyl form. However, they are dynamic and typically must be of low molecular weight in order to have some solution stability. New methods of preparing one-step phenolics in dispersion form have been described.<sup>36-39</sup> In the general reaction sequence, a two-stage reaction scheme is employed. Using alkali or alkaline earth metal hydroxide catalysts, the resole is first brought to a molecular weight near its water insolubility point. Then a polysaccharide such as gum arabic, gum ghatti, hydroxyalkyl guar, or poly(vinyl chloride) is added as a protective colloid coating which controls the particle size and distribution. The reaction is then advanced to a high molecular weight. Dispersions have been carried out from weight average molecular weights of 800 to 46000.<sup>36</sup> Stability improvement data are given in Table 5.

The preparation of special particulate, heat

**Table 5. The comparison of Phenolic Thermospheres (PTS) to Bulk Resole Stability.<sup>a</sup>**

Resin	Rate Constant, day <sup>-1</sup>		
	25°C	40°C	60°C
PTS	0.003	0.029	0.67
Bulk resole	0.018	0.097	1.5

<sup>a</sup>Based on resin flow on a 60 degree inclined plane.

sensitive phenolic resins using a suspension polymerization has been described by Brode.<sup>27,28</sup> These materials are reacted using phenol, aqueous formaldehyde, HMTA, and a suspension component such as gum arabic. A solid material results that has good thermal stability and is not so sensitive to water.

GPC studies indicate that a higher molecular weight material with a controllable narrow spherical particle distribution can be formed. Table 6 compares the  $T_g$  of a particulate resole to a bulk resole and a novolak. The particulate  $T_g$  is 48-54°C. Typical solid resoles have  $T_g$  around 40°C. The microstructure determined from <sup>13</sup>C NMR showed less methylol functionality and increased benzylamine and methylene bridges as compared to conventional bulk resoles.

### Resin Cure

The novolak resins are cured with *hexamethylenetetramine* (HMTA) or with the addition of resoles, or in many applications are modified with epoxy resins to promote special properties and an alternate mechanism for curing. HMTA is the most widely added curing agent and is used in the 5-15% range. With heat and moisture, HMTA breaks down stoichiometrically into ammonia and formaldehyde. The methylene bridge is the predominant linkage that is formed from the formaldehyde, and although most of the ammonia gas escapes, there are studies showing the formation of benzoxazines and azomethines.<sup>12</sup> These are thought to be responsible for the yellow color of HMTA-cured novolak resins.

The resole resins are thermoset materials that are cured with the addition of heat and pressure. The rate of curing these typically low number average molecular weight resins de-

**Table 6. Comparison of Phenolic Thermospheres (PTS)  
Glass Transition Temperature to Other Phenolics.**

<i>Resin</i>	<i>T<sub>g</sub>, °C</i>	<i>Wt% Gain, 22 °C</i>	<i>Form</i>
PTS	48–54	2.5–3.5	slightly sintered
Bulk resole	33–43	7.2–8.4	fused
Novolak	58–74	5.7–6.5	fused

depends on the temperature and on the distribution of polyols present. In fact, depending on which cooking program and what initial mole ratio is used, considerable variation in molecular weight and molecular weight distribution can be achieved in a controlled manner. This in turn influences the curing properties. The crosslinking reactions proceed primarily through the condensation of methylol groups and the splitting out of formaldehyde and water. Resoles that are catalyzed by ammonia will have nitrogen built into the bonding along with the methylene groups.<sup>15</sup>

### Resin Analysis

In recent years progress has been made in the quality control and molecular understanding of phenolic products through the use of modern instrumentation. Several tools that have been especially helpful in correlating structure and general properties are high and low field <sup>13</sup>C and <sup>1</sup>H FTNMR, gel permeation chromatography, differential scanning calorimetry, thermal gravimetric analysis, and dynamic mechanical analysis. In addition, Fourier Transform infrared spectroscopy (FTIR) is coming into much use.<sup>40,41</sup>

Nuclear magnetic resonance (NMR) measures changes in the electronic environment of a nucleus and consequently is related to the nature of the atom grouping and bonding in a molecule. The results are reported as chemical shifts  $\delta$  relative to a standard like tetramethylsilane. Integrated areas under absorption peaks can be related to reaction advancement and distribution of substitution. Early work done by NMR<sup>21,42</sup> has been followed by solid <sup>13</sup>C FTNMR studies making use of the magic angle technique on the thermal decomposition of cured resole phenolics<sup>43</sup> and the HMTA curing of phenolic resins.<sup>44</sup> Additional normal field

<sup>13</sup>C NMR studies include spectral assignments in PF resins,<sup>45–47</sup> benzylphenols<sup>48</sup> and cresol novolaks,<sup>49</sup> reaction curing,<sup>50</sup> and phenolic precursors.<sup>51</sup> Several very useful chemical shifts for novolaks dissolved in pyridine are for the methylene protons, *p-p'* at 3.8 ppm, *o-o'* at 4.1 ppm, and the *o-p'* substitution at 4.5 ppm. The areas under the absorption peaks allow the percentage distribution of isomers to be evaluated. The analogous <sup>13</sup>C signals are in the regions of 41.0, 30.8–31.4, and 35.5–35.9 ppm, respectively.

Gel permeation chromatography (GPC) measures flow retention volumes through a column packed with material of given pore sizes. Results proportional to molecular volume can be correlated to number average and weight average molecular weights, thereby allowing comparisons of molecular weight distributions and molecular weights.<sup>52–55</sup> These molecular weights are valid to the extent that a standard calibration curve represents the hydrodynamic volume characteristics of the polymer in question. Most laboratories have used polystyrene standards, which present some problems in arriving at reliable molecular weights for phenolics, especially resoles. The GPC methods using laser light scattering detection show promise for arriving at more accurate molecular weights and molecular weight distribution in phenolics.<sup>54</sup>

Differential thermal analysis or differential scanning calorimetry (dsc) measures the temperature change in a sample cell, generally relative to some inert standard, and can be run at fixed temperature versus time or as a function of temperature. Samples can be run under pressure. The areas under an exotherm or endotherm can be related to heat change, and consequently, in addition to melting points and *T<sub>g</sub>* values, parameters such as heats of fusion can be evaluated. The characterization of reaction

properties with dsc<sup>56-59</sup> and the importance of mechanical properties and glass transition temperatures can be obtained from dynamic mechanical analysis.<sup>60,61</sup> Solution dipole moments have also been used to examine novolak conformational properties.<sup>62,63</sup> These values follow a systematic function from a molecular weight of 200–6000.

## MANUFACTURE

Phenolic resins are typically made by the batch process in a stainless steel reaction kettle that is jacketed for steam or cooling water and equipped with a turbine blade or an agitator for stirring and a condenser. Molten phenol and formalin, typically 37–50 wt% formaldehyde, are charged into the kettle and agitation begun.

In *novolak* production an acid catalysis is added, and steam is applied to bring the reaction to a 100°C atmospheric reflux for 3–6 hours. The reaction time depends upon the catalysis, pH, and phenol mole ratio. At the end of the reaction time the load is dehydrated under atmospheric and then vacuum conditions. The final temperature reached under 25–27 inches vacuum is 140–160°C, which allows the residue phenol to be removed. The solid resin is discharged to pans or to a resin flaker. The resin can be sold in lump, powder, or flake form. Most resins sold in solid form are blended with HMTA before packaging.

In the manufacture of solid and liquid *resole* resins, the reaction procedure makes use of the exothermic nature for heat production and vacuum dehydration for temperature control. After the alkaline catalyst (which is usually sodium hydroxide, but sometimes calcium hydroxide, barium hydroxide or ammonia) is added to the phenol and formaldehyde, the mixture is allowed to heat at 80–100°C for 1–3 hours. The size of the kettle batch, for example, 60,000–135,000 lb, is controlled by the exothermic nature of the reaction, which has been measured<sup>64,65</sup> at 81.1 and 82.3 kJ/mole, the design of the reactor and the condenser cooling capacity.

Resole resins can set up in the kettle, so care must be taken to control the reaction. Reaction temperatures below 100°C are controlled by vacuum, and final dehydration temperatures are

kept below 105°C for resins used outside the wood adhesives industry. Low molecular weight water-soluble resins must be finished at low temperatures, 50–60°C, whereas less reactive *p*-substituted phenols can be finished at temperatures as high as 120°C.<sup>2</sup> Solid resoles are discharged from the reactor under rapid cooling.

In the manufacture of resole resins for the wood industry, the cooking procedure may have several loading steps for adding the formaldehyde or the base. Likewise, the temperature can be programmed to bring about different molecular weight and substitution characteristics. Since the materials are always shipped in liquid form, reaction conditions are carefully controlled to balance resin advancement with resin stability. That is, the resin must have high reactivity for good press times, and yet have reasonable storage stability. It is easy for resins to be too reactive and to set up in shipping or in storage.

If substituted phenols are used, such as *p*-*t*-butylphenol, the synthesis may call for the addition of an aromatic solvent and neutralization of the water layer.

## ABRASIVES

Phenolics are used in two main categories of abrasives. *Bonded abrasives* are three-dimensional structures such as grinding wheels and snagging wheels, and *coated abrasives* include sandpaper, sanding discs, and belts. According to the data reported in Table 1, the markets for abrasives have decreased by 11 million lb during the years from 1983 to 1987.

### Bonded Abrasives

Although the ceramic binders in bonded abrasives are generally harder and can be used in close tolerance work, the phenolic binders are tougher and can better withstand thermal and mechanical shock. The two main abrasives that are used in grinding wheels are aluminum oxide and silicon carbide. However, titanium oxide can be added to aluminum oxide for toughness enhancement, and an alloy of zirconium oxide and aluminum oxide developed by the Norton Company is important in heavy

duty grinding. The invention of silicon carbide by Dr. Edward Acheson in 1891 and the formation of the Carborundum Company gave birth to the modern abrasives industry. Now manufactured abrasives can be produced with selective uniformity from sizes 6000 fine to 6 coarse.<sup>66,67</sup>

The phenolic resin binder consists of a powdered two-step novolak resin. The amount of HMTA added (5–14%) depends on the final application of the grinding wheel. The resin can be used alone but is more frequently combined with a liquid resole or a furfural resin which sets the abrasives in place. Phenolics can be modified with epoxy resins and formulated in wheels to soften the grinding action. Modification with polyvinyl acetate and polyvinyl butyral can give a grinding action similar to shellac-bonded wheels which are useful in roll grinding.<sup>68</sup> Fillers such as cryolite ( $\text{Na}_3\text{AlF}_6$ ), potassium fluoroborate ( $\text{KBF}_4$ ) or iron disulfide ( $\text{FeS}_2$ ) melt at the grinding interface and act as lubricating agents. The phenolics used are fully cured at 150–200°C, so there is no danger of resin-filler interaction. The design of the phenolic, both in terms of molecular weight and the amount of HMTA that would be used, depends on the final application of the grinding or snagging wheel. High molecular weight phenolics used in conjunction with larger amounts of HMTA are needed for high speed or tough grinding applications where high heat resistance is needed<sup>2</sup> to withstand wheel surface temperatures that can reach 1200°C. On the other hand, if a lower molecular weight resin and lower HMTA content are important, a better wetting of the abrasive grain is needed. This also gives a grinding tool with better water resistance. The use of siloxane-coated abrasives can help water resistance, too.

The manufacture typically begins by first wetting each abrasive grain with a liquid resole resin. This will allow the powdered phenolic resin to coat and adhere to each grain. In some cases the abrasive can be coated with furfural, and the amount of HMTA added to the phenolic will depend on the amount of furfural used.<sup>69</sup>

The grading of the grinding wheel is very important. The grade of a wheel is designated by letters, ranging from A, a very soft grade, to

Z, extra hard. A hard wheel will have a larger amount of resin present, and more complete curing. The ratio of wet to dry resin is very critical and must be carefully controlled in order to handle the material as it is placed in the steel mold. It is important to preserve uniformity in the mixture and to prevent agglomeration in the mold. Wheels can be cold pressed, which is most economical, or hot pressed at temperatures generally between 175 and 205°C.

### Coated Abrasives

Phenolic resins are the primary adhesive used in coated abrasives, more commonly called *sandpapers*, found in the form of papers, belts, discs and drums. The resins used are typically formulated as one-step phenolic resoles made with a range of F/P ratios > 1. If the mole ratio is high, the resin will have high methylol content, enormous water solubility, allowing 50–75% solutions prepared with pH 8 and above, and fast cure at temperatures around 93–104°C. The resins in the intermediate mole ratio area, pH 6–8, run at 75–88% solids, have low water miscibility, and cure in the 135–149°C range. The lower mole ratio resins prepared near pH 8 have much less methylol content and therefore cure more slowly and require relatively high curing temperatures, e.g., 115–130°C. A recent patent<sup>70</sup> describes a binder that is fast curing at a low temperature of 130°C. This binder contains a phenolic resole in conjunction with mixed condensates of mono and polyhydric phenols and formaldehyde reacted in an F/P mole ratio typically in the 1.3–1.8 range at lower temperature, e.g., 40–80°C. The binder is said to have low free formaldehyde present and excellent resin storage stability.

The selection of resin type or blend of resins depends on the type of paper being coated, the kind and size of the abrasive grit used, and the parameters for the optimization of production time.

The abrasives used for coatings are diamond, aluminum oxide (corundum), silicon carbide, boron carbide, boron nitride, emery, flint (quartz), and garnet. These range in hardness and cost. Typically the superabrasives, synthetic diamond and cubic boron nitride, do not compete easily with the standard abrasives,

aluminum oxide and silicon carbide.<sup>71</sup> Flint is a quartz material and found throughout the United States, but the high quality forms are mostly from New Hampshire and Maryland. Garnets are silicates of varying color and quality. They are harder and tougher than flint. Other specialty abrasives are chromium oxide used to polish stainless steel, and zirconium oxide used for glass polishing.

Testing of coated abrasives must be done primarily by running plant trials and examining the end-use performance. However, some standard tests include hot and cold tensile and flexural strength, resistance to water or coolant, maximum speed characteristics, and grinding efficiency ratio, i.e., metal removal versus wheel wear.

## COATINGS

Phenolic resins play an important role in the coatings industry because of their ability to react with epoxy, alkyd, natural resins and maleinized oils for tailored protective coating applications. Modified phenolics are important as water, moisture, or solvent vapor barriers and they can generally protect metals from a corrosive environment. Unmodified phenolics are not good for coatings because of inherent tendencies for discoloration as well as the stiffness resulting from the rigid, three-dimensional structure in the cured state. However, when they are combined with, e.g., an epoxy resin, a good balance of properties is obtained. They are used mostly for undercoatings or coatings that are colored. A good review of phenolic coatings is given by Richardson and Wertz.<sup>72</sup> The area of protective coatings has grown 27% since 1983, although it has been relatively constant the last three years. See Table 1.

Phenolics such as novolaks can easily react with epoxides through the phenol hydroxyl group, using only heat and a base catalyst. The degree of crosslinking and flexibility introduced into the resin is controlled by the nature of the epoxide. In this reaction no water is released, and relatively thick films can be formed without blistering or voids. Applications are in pipe linings and electrical insulation. An example of an electrical encapsulation formulation is given in Table 7. Resole materials can

**Table 7. Formulation for Electronic Encapsulation.**

<i>Constituent</i>	<i>Parts by Weight</i>
Epoxidized novolak	20
Phenolic resin	10
Silica flour	70
Lubricant (stearate)	1
Catalyst	0.4-2

react with higher molecular weight epoxides that contain both epoxide and hydroxyl functionality. Here, fast reactions requiring only heat occur through both the phenol hydroxyl and methylol moieties. These resole formulations are excellent for container coatings and primers where a high degree of flexibility is needed. A typical baking primer coating formulation is given in Table 8, and a primer formulation is shown in Table 9.

Rosin-modified phenolic resins are very useful in printing ink, oil lacquers, and in alkyd paint applications. A commonly used material consisting of rosin acids is colophonium that is

**Table 8. Baking Primer Coating Formulation.<sup>a</sup>**

<i>Constituent</i>	<i>Weight %</i>
UCAR Phenolic Resin BKR-2620	9.01
UCAR Phenoxyl Resin PKHH	3.15
Iron oxide, synthetic	12.16
Barytes	13.51
Zinc oxide	1.35
Methyl ethyl ketone	24.33
Cellosolve acetate <sup>b</sup>	24.33
Toluene	12.16

<sup>a</sup>Ref. 73.

<sup>b</sup>Union Carbide Corp. Trademark; the acetate of ethylene glycol monoethylether.

**Table 9. Epoxy/Phenolic Coating Primer.<sup>a</sup>**

<i>Constituent</i>	<i>Weight %</i>
Synthetic iron oxide	37.5
Epon-1007 (Shell Chemical)	17.5
UCAR phenolic resin BKR-2620	11.0
Toluene	15.7
Methyl propasol <sup>a</sup>	7.5
MEK	4.5
Methyl propasol acetate <sup>a</sup>	2.3
n-Butanol	4.0

<sup>a</sup>Union Carbide Corporation Tech. Bull.

<sup>b</sup>Union Carbide Corporation Trademark.

generally reacted with a resole phenolic in the molten state between 110 and 140°C. The reaction is finished at temperatures near 250°C.<sup>11</sup> Oleoresinous varnishes and alkyd-modified phenolics can be formulated that cure at room temperature and are relatively clear.<sup>73</sup>

Cresol-, xylene-, and phenol-formaldehyde resoles find importance in the electronics field application. These materials are made flexible with PVB, PVF and alkyds. They are used in impregnating, dynamo sheet, and wire varnish applications.

## FOUNDRY

Phenolic resins have been an important part of the foundry industry for many years. However, as can be seen in Table 1, the drop from 77 million lb in 1985 to 41 million lb in 1987 has followed economic changes in that industry.<sup>5</sup> Phenolic resins are used for binding the sand used in manufacturing shell molds and cores. The castings can be done either in permanent molds or lost molds. Permanent molds are typically made of metal or ceramics and are used primarily to cast low melting metals. Lost molds, used to cast ferrous metals, are made from sand and an inorganic binder such as clay and water or an organic binder such as a novolak two-step resin.

Although molds made with clay or sodium silicate binders are inexpensive, they have low dimensional tolerance and low stability. Phenolic resins used as binders have many good properties such as excellent dimensional stability, fast curing times, and excellent storage of cores and shells. In some applications furfuryl alcohol and urea formaldehyde resins are also used.<sup>74,75</sup>

Silica sands of very high purity are primarily used in sand molding operations. However, other materials can be added to control thermal expansion characteristics. Additional factors that are very important in forming the character of the mold are the sand grain and the size distribution. The shapes of silica sands, for example, are round, sub-angular, and angular. Round sands have more strength in the composite per resin content, but angular sands resist cracking. The rounded, low thermal expansion zircon is often added to silica sands to balance properties.<sup>74</sup> Sand properties are listed in Table 10.

Five basic fabrication processes are used by the foundry industry. These are the no-bake, cold-box, hot-box or warm-box, oven bake, and shell processes.<sup>74</sup>

**No Bake Process.** In this process the sand and binder components are in a curing state at room temperature. Shortly after the cure is underway, the core box is filled with the sand mix and as soon as the core becomes stable it is removed from the box. This may take only a few minutes or several hours.

**Cold-Box Process.** In the cold-box process which takes place at room temperature, a gas catalyst is passed through the sand to promote curing. The catalysts are triethylamine or methylethylamine for phenolic isocyanate binders, sulfur dioxide for vinyl-unsaturated urethane binders, and methyl formate for an alkali metal salt of a phenolic resole binder. High-*ortho* resins have been developed for the phenolic component by using water-free systems and salts of divalent metals as catalysts. A recent patent describes improvements in the two-package phe-

**Table 10. Properties of Inorganic Sands.<sup>a</sup>**

Property	Sands			
	Silica	Chromite	Zircon	Olivine
Composition	SiO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub> FeO	ZrSiO <sub>4</sub>	(Mg, Fe) <sub>2</sub> SiO <sub>4</sub>
Specific gravity	2.64	4.5	4.6	3.2
Thermal Exp., in./in.	0.018	0.005	0.003	0.0083
Heat transfer	ave.	very high	high	low
AFS grain <sup>b</sup>	25-180	50-90	95-160	40-160

<sup>a</sup>W. Rossbacher, Ref. 74.

<sup>b</sup>American Foundry Society Standards.

nolic polyisocyanate process where the novolak or resole A-stage is water free and the solvent is nonpolar.<sup>76</sup>

**Hot-Box and Warm-Box Processes.** In these two processes the sand mixture is coated with a liquid thermosetting binder which is thoroughly combined with the dry sand and a latent acid catalyst. This mixture is blown into the core box at a temperature from 100 to 260°C. Upon heating, the catalyst releases the acid which induces a rapid cure of the core. The core can be removed from the box in 10–30 seconds and the cure continues under the exothermic reaction. The hot-box method typically requires post-curing in an oven.

**Oven-Bake Process.** The oven-bake process is one of the oldest in the industry, and is least used. The resins used are made from unsaturated hydrocarbons and heavy oils.

**Shell Molding Process.** The process for combining resins and sand into a shell mold was invented in Germany and patented in 1944 by Johannes Croning. In the beginning 7–8% resin was mixed with the dry sand, but over the years this has been reduced to 1–4%. Novolaks are the main binder used in shell molding and are available in powder, flakes, granules, or as solvent- or water-borne materials. High-*ortho* novolak resins have wide application in this process because of their rapid curing rate.<sup>77</sup> The shell lubricant, usually calcium stearate, is added at 4–6% of resin weight and HMTA runs between 10–17%.<sup>78</sup> Initially, the sand is treated by one of several methods. It can be: (1) dry mixed with the powdered resin, HTMA and lubricant; (2) cold-coated with a powdered or an alcohol solution of novolak, HMTA, and lubricant; (3) warm-coated using warm air near 121°C and sand around 66°C; or (4) the hot-coated method where the sand is preheated to 140°C and then cooled to under 93°C with a water-borne novolak applied. The coated mix is then dumped on a hot pattern, forming the investment. After going through a short cure, the investment is inverted to remove excess sand, and then turned over and cured for an additional 1–3 minutes at 345–540°C. The mold shell is then stripped from the pattern. Gener-

ally speaking, the hot tensile strength continues to increase parabolically with the HMTA content up to 18%. In order to reduce some of the common shell problems such as mold cracking, peel back, soft mold, or low hot-tensile strength, other additives such as Vinsol (Hercules, Inc.—thermoplastic resin derived from pinewood), potassium fluoroborate or zircon are used. The variables of resin content, length of cure, percentage of HMTA, and mix of sands must all be controlled to optimize the process.

## FRICITION COMPOSITES

Phenolic resins are the primary binder for a variety of materials in the production of friction products used mainly in the automotive industry such as brake linings, brake blocks, disk pads, clutch facings, and automatic transmission blades. Phenolic resins are important in these composites due to their thermal stability, resistance to solvents and nonflammability. After some decline, the phenolic resins friction elements market has been increasing over the past three years and is now at 29 million lb. See Table 1.

**Fillers.** In past years asbestos, especially chrysotile asbestos, was the main wearing filler for friction products. It gave an even, powdered breakdown of the friction element and had even friction properties with increasing temperature. However, with the clear physiological and carcinogenic hazards of all four asbestoses—chrysotile, crocidolite, amosite, and anthophyllite—work has been accelerated to find substitutes.<sup>79–81</sup> This has proven to be challenging and costly since no one material has all the same properties as did asbestos, so in many cases a mixture of materials is needed.<sup>79</sup> Mineral, carbon, aramid, and metal fibers are increasingly being used as replacements for asbestos. A newer material developed by Jim Walters Resources<sup>79</sup> is a processed mineral fiber called PMF. PMF is a single-strand, fibrous material that has shown considerable promise in this area. Many brake linings using the DuPont aromatic amide called Kevlar are in use. A recent patent<sup>82</sup> discloses a friction material composed of 5–70% by weight of



pulplike particles from heat-resistant polymeric aromatic amides. Other nonreinforcing fillers used are barium sulfate (barytes), rottenstone, and brass particles.

**Resins.** The phenolic resins used are varied. They are novolak, resole, novolak/resole combinations, cresol resins, and rubber-modified and oil-modified novolaks. Tung oil, cashew nut shell liquid (CNSL), linseed oil, and soya bean oil are reacted with phenolics. The value of oil-modified phenolics is the quieter performance of the braking action, and the reduction of cracking in components. Oil-modified novolak resins are supplied in viscous liquid or powdered forms. The flexibility in the cured resin can be controlled by the percentage and type of oil introduced into the resin.

Cresylic acid, which is a mixture of cresols, phenol, and xylenols, is also used in resins. This material can be purchased from technical grades with 80–85% of a particular constituent to 98% single component purity. A typical oil-soluble phenolic resin can be made from *p*-*t*-amylphenol employing an acid catalyst. Both *p*-*t*-butylphenol and *p*-*t*-octylphenol have applications here, too. If these materials are first reacted with an alkaline catalyst, then the initial resole formulation can be modified with unsaturated compounds such as drying oils, rosins, and rubber.

**Manufacturing.** Several of the main processes include impregnation of the asbestos or glass fabric for linings and clutch facings, the wet mix dough process for drum brake linings, and finally the dry mix process for disk brakes and drum linings. In the impregnation process, a B-stage resin is pressure-driven into the fabric. The dry mix process is the most heat-resistant type and is made for heavy duty truck applications. The powdered phenolic novolak resin as well as liquid and powdered resoles are mechanically mixed with the fiber (asbestos or Kevlar) along with the other fillers and friction components. It is first cold pressed and finally hot pressed at higher pressures and temperatures of 125–135°C. Details of processing are found in Barth.<sup>2</sup> A two-binder friction composition has recently been patented.<sup>83</sup>

**Testing.** Although there are no industry product standards for brake linings and each company establishes its own specifications for particular markets, the Society of Automotive Engineers (SAE) has set standard test methods. Performance tests determine friction and wear parameters. There is an SAE J-661 Brake Lining Test Control Procedure which uses a standard Chase-type friction testing machine. However, modern analytical methods using electron microscopy, differential scanning calorimetry, thermal gravimetric analysis and measurement of the coefficient of thermal expansion, heat capacity and modulus of elasticity are found to be important. A recent article by Lambla and Vo on optimizing friction materials is of interest here.<sup>84</sup>

## MOLDING COMPOUNDS

All phenolic molding compounds are resins that are reinforced with minerals, glass fibers, aramid fibers or carbon materials. The binding and adhesive nature of the phenolic with the fillers plays an important role in the final structural properties. These composites when fully crosslinked can withstand high temperatures under high load for long periods of time; see Table 11.<sup>85,86</sup> Phenolics as a class are non-flammable, and when burning give off very little smoke. Applications range from electrical and electronic components such as electrical sockets and printed circuit boards to automotive, such as distributor caps, relays and brake pistons; to housewares, such as utensil handles and appliance parts; and to sheet molding materials such as those used for instrument panels and airplane interiors.

The amount of phenolics used in molding processes has declined; but there is substantial interest in the electrical/electronics market<sup>87</sup> since phenolics can form matrices to withstand considerable mechanical stress while retaining thermal stability.

The novolak phenolic is the most commonly used in these applications because of its longer shelf-life. Resole resins, however, have the advantage of not emitting ammonia during molding or operation in a closed, high-temperature environment. They also retain their dimen-

**Table 11. Load and Heat Deflection for Engineering Plastics.**

<i>Material</i>	<i>Maximum Stress Load, psi</i>	<i>Temp., °C</i>	<i>Deflection, degrees, 4 hr</i>
Polysulfone, 30% glass	1,050	175	5
Polybutylene terephthalate, 30% glass	525	200	9
Polybutylene terephthalate, glass/ mineral	525	200	9
Polyethylene terephthalate, 30% glass	1,050	210	8
Polyether-imide, 10% glass	1,050	210	8
Polyether-imide, 20% mineral	275	210	5
Polyether sulfone, 30% glass	275	205	7
Polyphenylene sulfide, 30% glass	275	260	4
Polyphenylene sulfide, glass/ mineral	275	260	4
Phenolic, mineral filled	2,100	210	4
Thermoset polyester glass/min- eral	2,100	230	3
Thermoset polyester BMC 30% glass	2,100	260	2
Phenolic, 20% glass <sup>a</sup>	2,100	270	1

<sup>a</sup>Deflection of 4° at 285° after 500 hr, Plenco 06582.

sional stability during vapor-phase soldering conditions, and expansion and swelling at higher temperature are minimal.<sup>88</sup> Novolak phenolics also do well here if the entrapped gases are driven off by post-curing.

**Resins.** Novolaks cured with HMTA are the principal resins used in composites. The resin and the curing agent make up between 30 and 50% of the composition. Sometimes the resin is modified with as much as 10% melamines. Resins are typically cured with oxalic acid, although hydrochloric or sulfuric acids are used, too. High-*ortho* novolaks find use in a number of applications. One-step resoles or resole/novolak combinations also find use in specialty applications such as glass fiber compounds or compounds that need to adhere to copper substrates in electrical products. In this latter case, the use of non-ammonia-producing cures is essential, since ammonia attacks the copper. Novolaks cured with epoxide resins are important where gas generation cannot be tolerated. The inherent discoloring in the phenolic resins limits the possibility of making clear molded products; however, a variety of colored products are now being developed.

Great effort is continuing to extend the temperature range of phenolics. When compared to most engineering plastics, phenolics have a significantly higher glass transition temperature, e.g., around 200°C. It appears that the  $T_g$  can be increased to as high as 244°C by annealing molded parts.<sup>88</sup>

A phenolic resin which is modified with a thermoplastic elastomer<sup>89-91</sup> can function at 180° for 1600 hr with minimal weight loss, whereas a mineral-filled phenolic will show considerable weight loss.

**Fillers.** Fillers used in molding compounds are glass fibers, aromatic polyamide fibers (like Kevlar and Arenka), mineral flour (mica, silica, wollastonite, talcum, and calcium carbonate), wood flour, cellulose, and carbon fibers. Fillers reduce shrinkage during cure, give higher compressive strength and stiffness, and improve thermal resistance, electrical properties, and flame retardancy.

Calcium-aluminum silicate is the most used mineral filler because it is economical. Mica imparts high dielectric strength and thermal resistance, and also has low thermal conductance.<sup>11</sup> The high temperature and strength

characteristics of aramid fibers are bringing them into specialty markets. Fillers ranging from wollastonite to glass spheres, modified with silanes, titanates, and wetting agents,<sup>92</sup> are available from NyCo, a division of Processed Minerals Corp. Asbestos, because of its health hazards, is being phased out of the industry.

A typical mixture of a general molding compound is shown in Table 12, and a sheet molding formulation is given in Table 13. Sheet molding compounds are in increasing demand in automotive, transportation, construction and appliance markets. These phenolics are non-flammable and give off little smoke, unlike polyesters.<sup>93</sup> Substituted novolak structure-property relationships and flammability have been examined by Pearce.<sup>94</sup>

**Manufacturing.** Phenolic resins are molded mainly by injection, compression, and transfer molding. *Injection* molding is the dominant method. A new technique is *reaction injection* molding (RIM). In this method two or more reactive components are brought together under low pressure into a mixing stream and then forced into a hot mold. A phenolic RIM system developed by Brode, Chow and Michno<sup>95</sup> employs a high-*ortho*, high-solids, liquid resole resin that is combined with a latent acid catalyst like phenyl hydrogen maleate, phenyl trifluoroacetate, or butadiene sulfone.<sup>96,97</sup> Molded

parts from preformed glass mats were comparable to "vinyl esters" (epoxyl acrylates) and polyester materials, and displayed better thermal stability.<sup>98</sup>

Coefficients of thermal expansion are summarized by Mersereau.<sup>99</sup> Coefficients for phenolics filled with carbon are similar to steel over the range of temperatures from 20 to 160°C.<sup>99</sup>

**Post-Treatment.** A post-bake (post-curing) can have a beneficial effect on the thermal stability and dimensional stability of phenolic molded parts. Early work showed that the glass transition temperature ( $T_g$ ) increases with cure in phenolics.<sup>99-101</sup> More recently it has become apparent that the  $T_g$  of an as-molded phenolic novolak part strongly influences the post-bake conditions to be used. If parts are molded above the  $T_g$ , an unacceptable expansion can occur.<sup>102,103</sup> The  $T_g$  continues to increase during the post-baking. Table 14 gives data showing the changes of  $T_g$  with curing time and post-cure. This data suggests that the post-baking operation is best done in a series of programmed steps where the oven temperature is always a prescribed value below the glass transition temperature.<sup>102,103</sup> A computer model of post-baking has been put forth by Landi.<sup>104</sup>

Some new applications include the work the Rogers company is doing with Polimotor Research to build a totally plastic car engine based on a moldable phenolic composite. A plastic engine is in operation. Also, a compression molded military helmet has been made<sup>91,105</sup> from a catalyzed resin system composed of equal parts of phenolic and polyvinyl butyl resin impregnated into 19 layers of Kevlar aramid fiber. Composites made of Novoloid phenolic fibers in polypropylene, examined by Broutman,<sup>106</sup> showed an increased heat deflection temperature with only a small reduction in impact strength.

**Table 12. A Typical Compression Molding Compound Formulation.**

<i>Component</i>	<i>Weight %</i>
Phenol novolak	40
HMTA	6
MgO	1
Wood flour	50
Lubricant and release agents	1
Coolant and pigments	2

**Table 13. A General Sheet Molding Compound Formulation.**

<i>Constituent</i>	<i>Weight %</i>
Phenolic resin content	35-50
E-glass	25-40
Calcite (CaCO <sub>3</sub> )	10-20
Other Additives	2-10
Lubricants and release	1-3

## PHOTORESISTS AND CARBONLESS PAPER

**Resists.** Photoresists are light- or other energy-sensitive resins that can be applied as films and patterned to protect some and expose other areas of silicon wafers for doping, etching, or plating, using either positive or negative im-

**Table 14. The Change of  $T_g$  with Cure Temperature and Time.**

Cure Temp., °C	$T_g$ , °C					
	30 sec	60 sec	90 sec	180 sec	300 sec	1800 sec
132.2		87	98	115	122	
154.4	116	132	142	150	161	188
196.1	180	186	186		217	
218.3	207	214			242	

Post-bake (132.2°C) Schedule 90° to 232°,  $T_g$  = 287°C.

aging. In commercial microlithography, positive resists make use of the photofunctional change in diazonaphthoquinones in novolak resins since novolaks exhibit less swelling and image distortion during the development of the image than do negative materials. The novolak plays the role of the binder, holding the photoactive substance in place. Commercial positive resists usually are cresol-based. Molecular weight, molecular weight distribution and sample purity are very carefully controlled.

An improvement in photoresists for integrated circuit chips is the use of a multilayering effect to increase the resolution of smaller and smaller features. The top film layer receives the image to be transmitted through the other layers to the substrate surface. One application is to cover a film of conventional phenolic novolak photoresist with a second film of polystyrene doped with a nitron  $[R-CH=N(O)-R]$ . The nitron is opaque to light wavelengths from 315 nm well into the visible and is photolyzed at a shorter wavelength to a transparent compound. Light can then pass through the transparent areas to photolyze a 2-diazonaphthoquinone dispersed in the novolak to 1-indane carboxylic acid. The contrast-enhancing top film is stripped off with toluene-anisole solvent, and the image in the novolak is developed with aqueous alkali.<sup>108</sup> A *t*-butylphenol or phenylphenol novolak is used as the alkali soluble resin along with quinone-diazide or poly(2-methylpentane-1-sulfone) to make a positive resist with special radiation resistant crosslinking properties.<sup>109</sup>

Phenolic resin has been used to replace bisazide-cyclized polyisoprene through the incorporation of a variety of azides, giving a negative resist that is sensitive to broad areas of visible and UV light. A monoazide in-

creased the molecular weight or crosslinking through hydrogen abstraction.<sup>111</sup> A resorcinol-based novolak resin containing silicon as part of an alkyl ether linkage gave submicrometer images.<sup>107</sup> A positive resist incorporating as much as 50% trimethylsilylnitrile into a phenol-formaldehyde resin has also been described.<sup>110</sup>

In many cases phenolic resists have poly(*p*-vinyl phenol) as the matrix.<sup>112</sup> They are easily prepared from *p*-vinyl phenol and can be polymerized under free radical conditions and crosslinked with HMTA<sup>113</sup> or epoxide resins.<sup>114</sup> They can also be used in combination with epoxide resins in the production of multilayer circuit boards.

**Carbonless Paper.** Novolaks based on *p*-phenylphenol and other *p*-alkyl phenol copolymers have proven to be valuable in the manufacture of carbonless paper. In order to keep the oxidation and yellowing of the papers low, highly hindered substituted alkyl phenolics are incorporated as antioxidants. New formulations also incorporate the phenolics as zinc and aluminum salts.

The process that occurs arises from an electron transfer between an electron donating organic compound and a color developing material such as crystal violet lactone or benzoyl leucoauramine dyes. The phenolics act as coating materials.

## LAMINATING

Phenolic resins have been successfully applied in the manufacturing of electronics materials, decorative laminates, filters, and tubes. The resin easily penetrates papers of various kinds because of the hydrophilic nature of the resins. Most laminating processes make use of resole

type materials with high percentages of methanol groups present.

**Electrical and Industrial.** The large demand for electrical components that have high heat resistance under load, excellent flame retardance, and good mechanical properties along with an attractive price, have brought growth to industrial laminates made with phenolics. A Vits high-speed saturated paper treater is shown in Fig. 1. The impregnation of papers, cloth fabrics such as cotton, glass, and carbon fiber mats has standards documented in the LI-1 NEMA code (National Electrical Manufacturers Association)<sup>115,116</sup> in the United States, the DIN 7735 code in West Germany and the NF in France. Some of the NEMA standards for paper and glass are given in Table 15. The NEMA code was revised in 1983 and is again undergoing revision, to be released in November, 1988.<sup>117</sup> Since people in the marketplace are always looking for better materials and higher performance, the higher standard grades are always in a state of change. A study has been done on carbon laminates by NASA to

characterize the phenol formaldehyde resin properties.<sup>118</sup>

**Resins.** For economic reasons, the one-step impregnation of material is preferred. However, with kraft papers, for example, a two-step resin impregnation is needed if the machine line is not long enough. The resins are all resoles typically composed of phenol-, cresol-, or xylenol-formaldehydes with *p-t*-butyl- or *p-non*-ylphenol inserted to enhance flexibility. Phenol resins can even be modified with other synthetic flexibilizers, e.g., polyethers, polyesters, or polyurethanes. The resins must be carefully controlled in molecular weight and molecular weight distribution. Metal ions must be kept at minute concentrations, which dictates that cations from basic catalysis must be precipitated at the end of the reaction. Thus it is convenient to use calcium, barium, or magnesium hydroxides for the resole preparation which allow the cation to be eliminated as an insoluble sulfate. In a two-step impregnation such as would be required for a kraft paper, the first step requires a low molecular weight resin

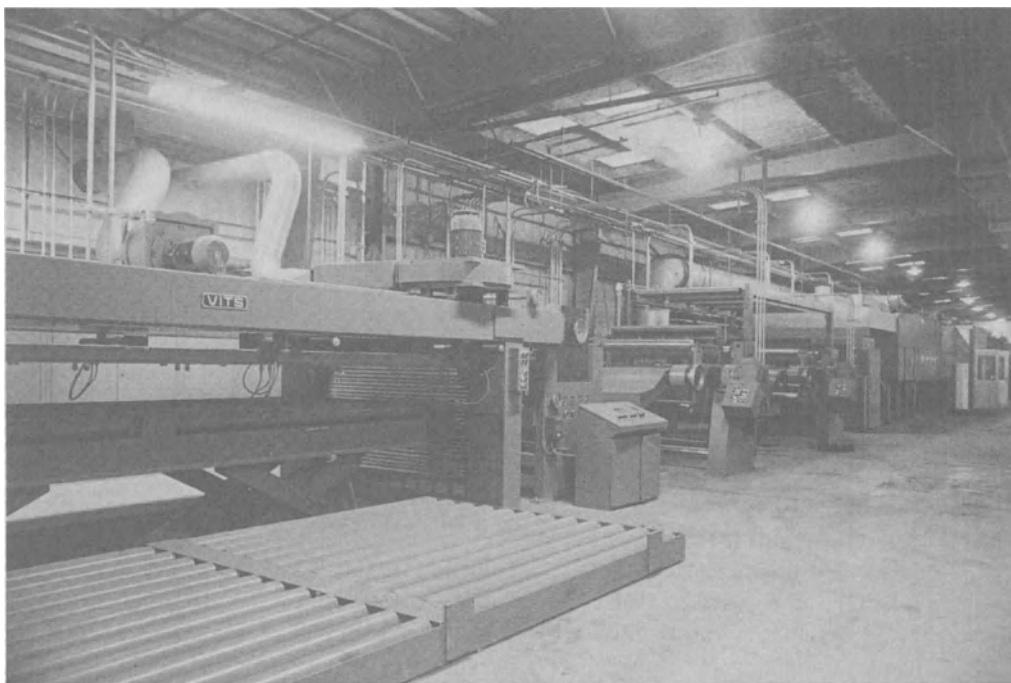


Fig. 1. The sheeter and roll winding stations on a Vits (W. Germany) high-speed phenolic saturated paper treater. (Courtesy of Reichhold Chemicals, Inc.).

**Table 15. NEMA LI-1 Laminated Thermoset Sheet Grades.<sup>a</sup>**

NEMA Grade	Description	Reinforcement <sup>b</sup>	Resin Content, %
X	mechanical	kraft paper	33–36
XP	hot punching	kraft paper	33–38
XPC	cold punching, weaker than grade XP	kraft, acp, clp	34–40
XX	normal electrical	clp, acp, bp	45–50
XXP	hot punching, better than XX in electrical prop.	clp and acp	45–50
XXX	radio frequency work, moisture resistance	rag pap, acp, clp	55–60
XXXX	good electrical, good insulation, and low dielectric loss under high humidity	rag, acp, clp	57–60
XXXPC	same as XXXP except suitable for cold punching	rag, acp, clp	57–60
XXXPC/FR-2	class I flame resist.	rag, acp, clp	57–60
C	gear stock and high impact applications	cotton fabric	46–50
CE	electrical properties nearly equal to XX	cotton fabric	50–55
L	fine machining props	cotton fabric	46–50
G-3	high impact and flex strength, good electrical	continuous fil. glass fabric	55–60
N-1	excellent electrical	nylon fabric	55–60

<sup>a</sup>Adapted and revised from Ref. 2.<sup>b</sup>Legend: acp = alpha = cellulose paper; clp = cotton linter paper; bp = bleached kraft.

with high solids. The second resin application must introduce the flexibilizers into the paper. Tung oil is a good material for modifying the resin since it brings in flexibility and toughness. The final board has good punchability and is solvent resistant.

The production of a low-colored laminating resin is described in a patent issued to Weyerhaeuser.<sup>119</sup> The resin is made with an F/P mole ratio in the range of 1.9–5.0 using citric acid to neutralize the mixture. The distribution of formaldehyde in this material as determined by

NMR is shown in Table 16. A phenolic resin composition patented by Hitachi<sup>120</sup>, based on a brominated cresol novolak, meets UL V-1 fire resistance ratings. Another area where considerable development has taken place is in modifying phenolics with epoxy resins for use in items ranging from circuit boards to recreational equipment.

**Decorative Laminates.** The main application here is in the furniture and cabinet markets. As can be seen in examining the

**Table 16. Distribution of Formaldehyde in Uncured Resin Intermediate.**

F/P	Li <sub>2</sub> CO <sub>3</sub> <sup>a</sup>	Distribution of Formaldehyde, Mole %				
		—CH <sub>2</sub> OCH <sub>2</sub> OH	—CH <sub>2</sub> OCH <sub>2</sub> —	—CH <sub>2</sub> OH	—CH <sub>2</sub> —	H <sub>2</sub> CO
2.00	0.55	32.8	6.6	38.3	10.8	11.5
2.65	0.76	36.2	8.4	20.5	16.9	18.1
3.14	1.12	34.4	7.8	27.7	15.9	14.6
5.00	1.47	37.4	5.1	9.4	10.1	38.0

<sup>a</sup>Moles to moles phenol.

laminating products shown in Table 1, these markets have been strong and are growing. The high pressure laminating processes are applied in furniture production, and the low pressure process for decorative papers, wood veneers, and vinyl facings that are used in the lamination of particle board. The laminate in a paper application is produced by impregnating the paper with an A-stage resin, and then bringing it to the B-stage in cure with heat treatment as the solvent is removed. The final standard for these laminates is NEMA LD-3, 1985.<sup>121</sup> Generally NaOH-catalyzed phenol-formaldehyde resins are used, although some cresols can also be incorporated. The resin solids pickup is typically 32–35% based on dry paper. Melamine resins are used to impregnate the overlay papers (50%) and decorative top papers (67%).

Some industrial applications include impregnated kraft papers used for overlay plywood, and fiber boards for use outdoors where protection from weather and abrasion is needed. Concrete forms are one example.

**Filters and Separators.** Impregnated phenolic resin papers have important application in making oil, fuel, and air filters for the transportation industry. Generally novolak phenolics are used in a volatile solvent like acetone or methanol. The HMTA is a constituent in the resin. The solution consists of around 65% resin solids and the material is applied in the amount of 20–30% by weight of paper. Another area of importance is the production of battery separators. These materials are impregnated papers that are cured to a designated porosity. The resole resins used are prepared with a relatively high F/P mole ratio and are applied in the low molecular weight A-stage.

## WOOD BONDING

The area of phenolic use that is by far the largest deals with wood bonding, for example, in producing plywood, finger joints, wafer board, chip board, and laminated beams. This is illustrated by the data in Table 1. In understanding the wood-glue bond, the wood structure must be taken into account. Wood is composed of 40–45% cellulose, 20–30% hemicellulose, and 20–30% lignin, along with natural resins and

tannin structures.<sup>122</sup> The lignin structures are composed of a variety of phenolic units based on coniferyl and sinapyl moieties.

The exact ratios of the main tree components vary among the tree species and from hardwood to softwood. The structure of the lignin also varies. Although the exact nature of the bonds formed between the wood and the resin are not clearly proven, it is thought that there are several operating variables. These are the degree of penetration of the resin into the wood structure, the potential for hydrogen bonding interaction, and the reaction of reactive methylol groups with active functionalities within the lignin structures. In gluing operations the moisture content of the wood and the surface properties, such as porosity and coarseness, play an important role in the final bond formation. These factors can lead to the necessity of varying the glue mixes during the different seasons of the year.

**Plywood.** Plywood is a laminated structure that is composed of a minimum of three sheets of veneer layered cross-grain. It is used for construction siding, concrete forms, kitchen and bathroom cabinets, flooring, and roofing. The plywood resins must be tailored to the particular wood species being glued. For example, a formulation for exterior grade plywood based on douglas fir or hemlock is shown in Table 17. The resin is almost always based on phenol using a mole ratio of 1.5–2.5 F/P with a sodium hydroxide catalyst. Wheat flour is commonly used for a filler and walnut shell as an extender that helps control moisture dissipation from the glue line. Sometimes borax and blood are added for prepressing properties. The resins are generally 40–45% nonvolatiles and range from 25 to 31% solid weight in the final glue mix. Soda ash is included as a curing rate additive. Resins are currently made with very low free formaldehyde or free phenol present. However, much formaldehyde may be tied up as hemiformals. Glue mixes for other wood species must be formulated in very specific ways. If formulated, for example, for U.S. southern pine, variations of resole mole ratio, pH, fillers, and extender would be tried until the wood-glue bond was maximized in that wood species.

**Table 17. Exterior Plywood Glue Mix Formulation.**

<i>Constituent</i>	<i>Mix 1, Wt%</i>	<i>Mix 2, Wt%</i>
Resole resin	58.3 (43% NV)	62.5 (40% NV)
Water	21.2	19.5
Glufil HL <sup>a</sup>	11.0	—
Bohemia 100 <sup>b</sup>	—	11.6
Wheat flour	4.7	6.3
50% Caustic	4.7	—
Soda ash	4.7	—
Brookfield viscosity	4,100	4,800
pH	12.5	12.5
Veneer temp., °F	70	70
Wood failure %, 6.25 min press time @ 150°C	95	93

<sup>a</sup>Agrashell, Inc. Tradename for walnut shell flour.<sup>b</sup>Bohemia, Inc. Tradename for fractionated douglas fir bark.

When plywood is laid up in a 5-ply construction, first the back is placed down with the grain parallel to the long axis. The next veneer, called the *cross band*, has adhesive on both sides and is placed with the grain perpendicular to the back. Then the next veneer is placed with the grain parallel with the back, followed by another cross band with adhesive on both sides. The final top piece, like the back, has the grain parallel with the long axis. Then follows a stand time or a prepressing time to bring the glue into intimate contact with the surfaces before the hot pressing that will take place—5–7 min at 140°C and 175–200 psi for softwood plywood. Control of molecular weight of the resin, mix viscosity, and moisture in the wood are all important in setting a good glue line. A number of methods for extending the phenolic resin in wood bonding have been explored; for example, bark extender phenolic with the finely ground wood bark treated with aqueous alkaline phenol-aldehyde resin.<sup>123</sup>

**Composition Board.** In this class of materials are strand board, wafer board, chip board, particle board, and fiber board. As large-dimensional trees have become more scarce, a momentum toward research in developing and using composition board has increased. *Wafer board* is a construction that is competitive with plywood in many applications. It is made by spraying large wood particles with a resole resin in a rotating drum, usually at 2.5–3.0% of dry

wafer weight. The mixture is then molded under high pressure to achieve satisfactory weather-resistant bond strength. A recent patent has perfected the spray-drying process with good dry resin particle size control.<sup>124</sup> When the wood wafers are oriented by using a scattering grid or have chips with greater length than width, the product is called a *strand board*. These materials are made with higher resin content through use of liquid resoles, and have properties approaching those of plywood. In the United States, particle board is generally made with urea or urea melamine resins. However, because of the formaldehyde release problem with particle board, considerable work has been done with diisocyanates. These materials have excellent water resistant properties as compared to nitrogen resins.

**Laminated Beams.** Laminated beams or timbers are made using three or more pieces of sawed lumber with the grains laid nearly parallel. The adhesives are generally phenol-resorcinol- or resorcinol-formaldehyde mixes. These resins have rapid curing characteristics, excellent water resistance, and can be used in hot pressing or in cold curing. Mechanical systems allow the continuous spreading of the glue mix on sized, sawed lumber with the beams formed by stacking and clamping the timbers until room temperature cure has been achieved. Timbers can be treated with moisture and heat to be shaped into arches, for example.<sup>125</sup>



**End Joints and Finger Joints.** Another end use for fast curing resin is in end joints and finger joints. These are designed to build larger beams or to join pieces of lumber together with a strength that is greater than the wood strength. Resins have been developed that are two-component and very fast reacting when brought in contact with each other.<sup>126</sup> One component is a normal phenol-resorcinol-formaldehyde with a hardener like paraformaldehyde, and the second mixture contains a fast-reacting phenol-*m*-aminophenol-formaldehyde resin. When the components are brought together, for example, in mating two ends, a bond sets up in minutes, and is fully cured in 30 minutes at 25°C.<sup>12</sup>

A number of adhesives have been formulated by using either lignins or tannins in combination with phenolics for applications from plywood to composites.<sup>12</sup> Pretreatment of the lignin or tannin is a requisite to success in almost all cases. Generally it has been difficult to obtain consistent results. In addition, the products are not as water resistant as when prepared with PF resins.

## INSULATION AND FOAM

**Insulation.** Resole resins are sprayed on hot fibers with the matted fibers then heated until cured. The resins are generally phenol based and prepared at high F/P mole ratios, e.g., 2.5–3.5, and cooked at low temperatures. These conditions produce primarily uncondensed polymethylolated phenols. The catalysts are commonly alkaline earth hydroxides. The resin is applied in 10–15% aqueous solutions.<sup>11</sup> The PF resin imparts good dimensional quality to the glass wool mats and provides its important nonflammability characteristics.

**Foams.** Resins used in foam are made as resoles with an F/P mole ratio of 1.5–3.0 using either sodium or alkaline earth hydroxides. Formulations are made to contain approximately 80% resin solids. Foam density is regulated by the amount of surfactant, blowing agent, temperature and the acid-activity of the resin. Crosslinking is promoted by acids like *p*-toluenesulfonic or sulfonic acid. The foam blowing agent is typically a high-vapor-pressure liquid that is volatile under the exothermic

nature of the crosslinking reaction. Blowing agents can be chlorofluorohydrocarbons like trichlorotrifluoroethane or lower alkanes like pentane. With atmospheric ozone depletion becoming an international problem, fluorochlorohydrocarbons will need to be replaced.<sup>127</sup> Foam can be made in a cellular form which has great structural strength, or in an open, water absorbing form used in floral arrangements. With stricter flammability standards being formulated, interest will increase in phenolics.<sup>128</sup>

Phenolic microballoons are useful in making foams and other lightweight material. They can be molded with phenolics to form rigid syntactic foams that reduce weight, increase stiffness and improve crack resistance. They are used in floating devices, ablative heat shields for reentry vehicles, and cores for wall panels.<sup>129</sup> Honeycomb materials can now be made that have all the inherent strength of natural construction.<sup>130</sup>

## GENERAL ADHESIVES

**Contact Adhesives.** Phenolic resins are widely used in neoprene and nitrile contact adhesives mainly as tackifiers and adhesion promoters. That is, they are needed to help hold the material together while the main adhesion process takes place. Contact adhesives must have high green strength and high peel strength. Applications for these materials are in leather, cloth, plastic, and rubber adhesion, upholstery, weather stripping, and counter and desk tops. Phenolics used in neoprene contact adhesives are either substituted novolak or resole resins, whereas the nonsubstituted resole is primarily used with nitrile rubbers. A neoprene/phenolic formulation<sup>2</sup> is given in Table 18. A nitrile rubber contact adhesive could have 15% high molecular weight acrylonitrile rubber, 15% phenolic, and 70% of an oxy-solvent such as acetone. At 60°C this could have a canvas/canvas peel strength of 17 lb/in. after pressing for 15 min at 300 psi and 121°C. Other phenolic formulations are found in this book in the neoprene chapter. A good review of this subject was given by Barth.<sup>2</sup>

**Structural Adhesives.** Phenolic resins have had wide use in structural adhesives for their

**Table 18. A Neoprene/Phenolic Adhesive Test Formulation.<sup>2</sup>**

<i>Component</i>	<i>Parts by Weight</i>
Two-roll mill blend	
Neoprene AC	100
Neozone A antioxidant	2
MgO	4
ZnO	5
Phenolic resin	45
MgO	4
Water	1
Toluene	115
Hexane	115
Ethyl acetate	115
	<hr/> TOTAL 506
SOLIDS = 31.6% by weight	

strength properties with impervious substrates as well as with wood. They are combined with thermoplastic polymers to provide both metal-to-metal or metal-to-paper or plastic bonding. It is postulated that the phenolic crosslinks to rubber through quinone methide intermediates<sup>11</sup> by a 1-4 addition across the vinyl double bonds. Some of the main materials are NBR with 15-40% acrylonitrile in nitrile/phenolic resins and polyvinylacetal in vinyl/phenolic blends. In all cases the phenolic gives inherent strength, solvent resistance, and thermal stability to the adhesive.

## ENVIRONMENTAL AND TOXICOLOGICAL CONSIDERATIONS

When a phenol-formaldehyde resin is fully cured, there are few hazards connected with the material, although dermatitis has been reported.<sup>131,132</sup> However, the starting materials, phenol, substituted phenols, and formaldehyde, are hazardous. Consequently, when dealing with an A-stage or B-stage resin, there will be free formaldehyde and free phenol present in the mixture, and proper safety precautions should be taken. Phenols are highly toxic and can cause protein degeneration. Monomeric phenols can be quickly absorbed through the skin and cause a burning sensation and, in fact, considerable damage. The oral LD<sub>50</sub> for rats is 530 mg/kg. All phenolic resins containing more than 5% free phenol must be marked as poisonous, and those containing 1-5% as detrimental to health.

Although test results are not conclusive regarding the carcinogenic character of formaldehyde, it is known that many people are highly sensitive to this compound. The current standard in the United States for formaldehyde exposure on an 8-hr basis is 1 ppm time weighted average (TWA), 2 ppm short term exposure (STEL), and 0.5 ppm as the level where the company must take action.<sup>133</sup> In West Germany and Scandinavia the threshold limit value (TLV) is 1 ppm. Thermal oxidative breakdown products generated from phenolic resins have been examined by Waitkus and Lepeska.<sup>134</sup>

## PHENOLIC RESIN COMPANIES

Ashland Chemical Co.  
Columbus, OH 43200

BTL, Ltd.  
Niagara Falls, NY 14302

Borden, Inc.  
Salem OR 97300

CHEMBOND, Inc.  
Springfield, OR 97477

DuPont & Co., Inc.  
Wilmington, DE 19898

Fiberite Corp.  
Winona, MN 55987

General Electric Co.  
Pittsfield, MA 01201

Georgia Pacific Corporation  
Atlanta, GA 30348

Monsanto Co.  
St Louis, MO 63167

Occidental Corp.  
North Tonawanda, NY 14120

Plaslok Corp.  
Buffalo, NY 14200

Plastics Engineering Company  
Sheboygan, WI 53081

Resinoid  
Skokie, IL 60076

Rogers Corporation  
Rogers, CT 06263

Rogue Valley Polymer  
San Francisco, CA 94111

Schenectady Chemicals, Inc.  
Schenectady, NY 12301

Union Carbide Corporation  
Danbury, CT 06817

Westinghouse Electric Co.  
Hampton, SC 29924

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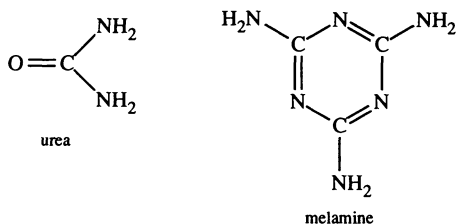
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# Amino Resin Adhesives

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Amino resins are prepared by reacting formaldehyde with a compound containing the amino group  $\text{—NH}_2$ . The amino compounds most commonly used are urea and melamine:



Urea-formaldehyde accounts for about 80% of production; melamine-formaldehyde constitutes most of the remainder. A few other amino compounds are used to a very minor extent.

Amino resins are manufactured throughout the industrialized world for a variety of applications. Adhesives represent by far the largest market. Large amounts of simple urea-formaldehyde resin adhesives are used to bond plywood and particleboard, also known as chipboard, flakeboard, or waferboard. More complex adhesive formulations are used to make laminated wood beams, parquet flooring and interior flush doors, and for furniture assembly.

Several large chemical companies manufacture a full line of amino resins. This may require as many as 75 different formulations to meet all application needs. Large particleboard manufacturers may prepare a simple urea-formaldehyde adhesive resin at the plant.

The principal attractions of amino resins are: water solubility before curing (which allows easy application to many substrates and with many other materials), colorlessness (which permits a colorless glue line as well as unlimited colorability with dyes and pigments), good solvent resistance, hardness, and heat resistance, as well as low cost. A limitation of amino resins is the release of formaldehyde during curing and in some cases after curing. Outdoor weatherability is poor for products made with urea-formaldehyde resins, but products made with melamine-formaldehyde resins have good water resistance and outdoor weatherability.

Some amino resins are used to modify the properties of other materials. For example, a small amount of an amino resin added to textile fabric imparts the familiar permanent press or wash-and-wear qualities. A small amount of an amino resin added to paper can improve the tear strength even when the paper is wet. Textile treating uses a low molecular weight soluble resin, whereas for paper treatment the resin is advanced to form a colloidal dispersion so that it will attach to the cellulose fibers as the paper is being made. The amino resin adhesive reacts with the primary hydroxyls of the cellulose, thereby replacing weak hydrogen bonds with strong covalent bonds. The hydrogen bonds are released when the paper or cotton fabric is wet, but the covalent bonds remain in effect so that the paper will retain strength and the cotton

fabric will return to the original creased or flat condition when dried.

## HISTORY

Urea-formaldehyde reaction products were described as early as 1908,<sup>1</sup> but the first useful commercial product, a molding compound invented in England by Edmond C. Rossiter,<sup>2</sup> did not arrive until almost 20 years later. It was a fairly complex formulation using purified cellulose fiber as reinforcement. The amino resin contained equimolar amounts of urea and thiourea. The new product could be supplied in light translucent colors. The molded products had a hard, stain resistant surface, and there was no objectionable phenolic odor. In short, the product was unique for its time.

Although the use of thiourea gave the moldings a better gloss and improved water resistance, it had the disadvantage of staining the steel molds. As the technology advanced it was found that the amount of thiourea could be reduced and finally eliminated. Today's urea-formaldehyde molding compounds contain no thiourea.

Melamine-formaldehyde resins were introduced about ten years after the urea-formaldehyde products came on the market. The Henkel Company was granted patents for products based on melamine in 1936 and 1937.<sup>3</sup> The products made with melamine-formaldehyde resin were very similar to those based on urea but with some important superiority. Molded plastics based on melamine-formaldehyde resin had much better water resistance and outdoor weatherability than moldings made with urea-formaldehyde resin. The combination of hardness, water resistance, and unlimited colorability made melamine-formaldehyde ideal for molded plastic dinnerware and this remains the major application. The good stability of the symmetrical triazine ring makes the melamine-formaldehyde polymers very resistant to chemical change once the resin has been cured to the insoluble cross-linked state.

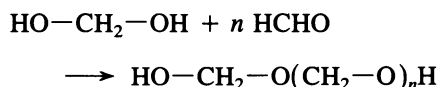
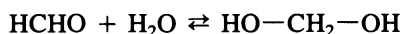
The use of urea-formaldehyde resin as an adhesive was suggested as early as 1918,<sup>4</sup> but since it offered no new desirable properties the commercial development was delayed until the amino-formaldehyde resin could compete on a

cost basis. It is interesting that in today's pattern of consumption, amino resin adhesives are by far the largest segment of the amino resin market. Reconstituted wood products such as plywood, chipboard, etc. represent the major use. Lack of water resistance and slow release of formaldehyde has been a deterrent to some applications.

The future of amino resins and plastics seems to be secure since they can provide qualities not easily obtained in other ways. New developments will probably be in more highly specialized formulations for specific applications.

## RAW MATERIALS

*Formaldehyde* is a highly reactive, pungent smelling, poisonous gas. It is made by passing air and methanol vapors through a heated copper or platinum gauze. The resulting formaldehyde is dissolved in water. It is highly reactive and can form methylene glycol:



The reaction can continue to produce chains of polyoxymethylene glycol. To prevent precipitation of the formaldehyde polymer, known as paraformaldehyde, the solution can be stabilized by adding methyl alcohol. A 37% solution of formaldehyde must be maintained at a temperature of at least 32° C to prevent precipitation of the polymer. By adding 5–10% methanol, the solution will remain clear if stored at room temperature.

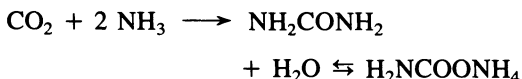
Higher concentrations of formaldehyde are often supplied to customers using large quantities of the chemical, to reduce shipping costs and improve manufacturing efficiency. Heated storage tanks are required. For example, at 50% formaldehyde the solution must be kept at 55°C to avoid precipitation. A very highly concentrated form of formaldehyde stabilized with urea is also available. It is manufactured by Allied Chemical Co. and is known as UF Concentrate 85.<sup>5</sup> The product contains 4.6 moles of formaldehyde for each mole of urea and is concentrated to 85% solids. It is convenient for

the manufacture of urea-formaldehyde adhesives, since the user need only add urea to give the desired urea-formaldehyde ratio, adjust the pH to the desired level, and react the resin to the desired state of cure before use in his specific application.

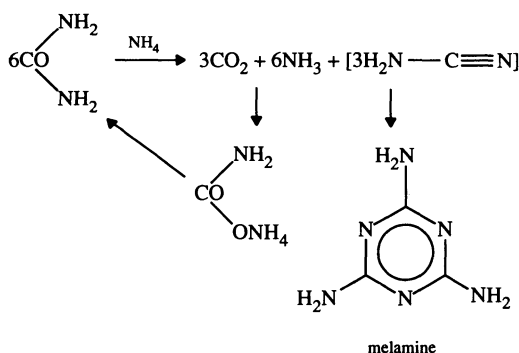
*Paraformaldehyde* is available as a solid in the form of flakes or powder. It is an unstable polymer and can easily release formaldehyde when dissolved in water. Formaldehyde also exists in the form of a cyclic trimer, *trioxane*. It is a fairly stable compound and is not used in the manufacture of amino resin adhesives.

*Urea* is the most important building block for amino resins and plastics—first, because urea-formaldehyde is the largest selling amino resin, and second because urea is used to make melamine, the amino compound in the second largest selling amino resin. Urea is also involved in the manufacture of a variety of other amino compounds that are also used to make amino resins.

Urea is a colorless, odorless solid, mp. 133°C. It is generally recognized as the first organic compound to be synthesized from inorganic raw materials; Wöhler synthesized it in 1828 by heating ammonium cyanate. Urea is now made in immense quantities for use as a fertilizer and cattle feed supplement. It is made by reacting carbon dioxide with ammonia under high pressure. Ammonium carbamate is first formed but releases a molecule of water to form urea:

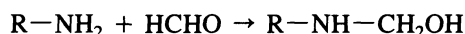


*Melamine* was synthesized early in the history of organic chemistry but remained a chemical curiosity until it was found to react with formaldehyde to form a useful amino resin. Melamine was first manufactured from dicyandiamide, but it is now made from urea, a much lower-cost starting material. In this process the urea is dehydrated to cyanamid which terminates to melamine. The reaction is carried out at high pressure in the presence of ammonia to suppress the formation of deamination products. Ammonium carbamate is also formed in the reaction and must be recycled to convert it back to urea.

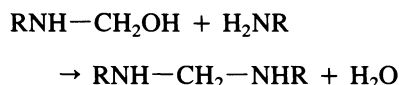


## CHEMISTRY

Two major chemical reactions are involved in the bonding of amino compounds together with formaldehyde to produce and cure an amino resin. The first is the addition of formaldehyde to the amino group to introduce the hydroxymethyl group, also known as the methylol group:



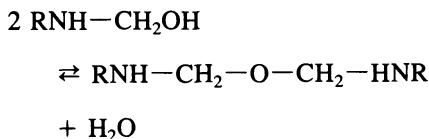
The second reaction is the combination of the methylol group with an active hydrogen to release a molecule of water forming a dimer, a polymer chain, or a vast three-dimensional polymer network. This reaction is known as methylene bridge formation, polymerization, or simply cure. It is illustrated in the equation below:



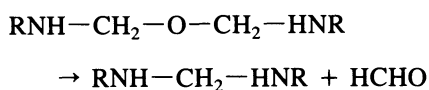
Success in making and using amino resins depends on the precise control of these two reactions. The first is primarily concerned with the manufacture of the resin, while the second is most important for the application in which the resin is used. The reaction of formaldehyde with an amino group will take place under either acidic or basic conditions. The second reaction, however is catalyzed by acid. It is common practice to prepare the resin under fairly neutral conditions. Both reactions can proceed slowly to form the methylol derivatives and advance the polymerization to the desired degree. Some polymerization is needed to



prevent crystallization of the monomeric methylol compounds. A possible side reaction is for two methylol compounds to combine forming a dimethylene ether linkage and releasing a molecule of water:



The dimethylene ether so formed is not as stable as the diaminomethylene bridge and may rearrange to form a methylene ether linkage and release a molecule of formaldehyde:



The methylol groups of amino resins may also react with the primary hydroxyl groups of cellulose. This reaction is of great importance in the use of amino resins to improve the wet strength of paper and to impart wash and wear qualities to garments made from cotton fabric. This reactivity of methylol groups may be of significance for the application of amino resin adhesives in the bonding of plywood and particleboard because it allows the formation of chemical bonds directly between the adhesive and the primary hydroxyl groups of the cellulose.

The usual catalysts or curing agents are ammonium salts, for example ammonium chloride. It may be mixed with wood flour or walnut shell flour and mixed with the amino resin just before application. A buffer may also be included with the catalyst. This could be calcium phosphate. It is slow in reacting but will combine with the acid released by the ammonium chloride and thus reduce the damage that the acid might cause to the wood. Such catalyst systems may be used with urea resins or urea-melamine resins to provide full cure at room temperature for furniture assembly. Resins for plywood and chipboard applications are usually hot pressed without any external catalyst.

Amino resins are usually made by a batch process. The ingredients are charged to a kettle, adjusted for pH, and heated to combine the

amino compound with formaldehyde and advance the polymerization to the desired degree. The excess water may then be removed by vacuum distillation to give the desired viscosity. Continuous processes have been described in patents and may be in use for making simple amino resin adhesives.<sup>6</sup>

## END USES

### Particleboard

Chips and shavings from scrap logs or from the processing of lumber are screened to the desired size. After drying to a moisture content of about 7%, the chips are coated with the resin adhesive, usually to about 7–9%, solids basis. The adhesive can be sprayed onto the chips as they tumble in a blender. A wax emulsion may also be applied to reduce the water absorption of the finished board. Total moisture content of the resin coated chips should be in the range of 8–12%. Too much moisture can cause blisters when the cured board is removed from the heated press. After application of the resin, the treated flakes are spread onto trays and formed into a mat which may be prepressed, and then loaded into a multiplaten heated press for curing. Cure time will depend on the thickness of the board and may be in the range of 10–20 minutes at a temperature of 125–175°C.

Three-layer chipboard is also produced, using fine particles treated with a higher resin content on the face layers, with larger chips in the core layer. The resulting chipboard may be 75% core and 25% surface layers.

Particle board made with urea formaldehyde resin adhesive is restricted to applications where it is protected from water. It may not be used in outdoor applications.

It is not uncommon to use a urea-formaldehyde resin of lower formaldehyde content in the manufacture of particle board. For example, the particle board adhesive might be 1 mol of urea to 1.8 mol of formaldehyde, while the plywood adhesive might contain 2 mol of formaldehyde for each mol of urea.

A variety of *formaldehyde scavengers* have been suggested for use in urea-formaldehyde resins for particle board. The addition of free urea or melamine just prior to curing the resin has been suggested. When the particle board is

subjected to hot weather and high humidity, the formaldehyde that is released might combine with these free amino compounds. However, the methylol compounds so produced might also undergo hydrolysis as hot and humid conditions are continued. Polyacrylamide has been suggested as an efficient scavenging agent for use in urea-formaldehyde adhesives.<sup>7</sup>

## Plywood

Plywood is an assembly of three or more layers of wood (veneers) joined together with an adhesive. Hardwood plywood has an outside layer of decorative wood such as walnut, oak, maple, etc. with interior or support layers of cheaper softwood such as pine. Ordinary plywood is 100% softwood and is used for structural applications only. It is usually made with phenolic resin adhesive to provide good water resistance. Hardwood plywood is made in both outdoor and indoor grades. The water resistant type is made with a melamine-formaldehyde adhesive that will not discolor a light decorative surface veneer. Phenolic resin can be used to provide good water resistance with dark colored veneers.

The adhesive is applied to both sides of the alternate ply veneers. They are passed through a glue spreader and then stacked between the uncoated veneers to form the plywood assembly. A product made with urea-formaldehyde adhesive might be pressed at 125°C and a pressure of 150–300 pounds per square inch for 5–10 minutes to achieve a satisfactory cure.

## High-Pressure Decorative Laminates

Melamine-formaldehyde resin provides both adhesive and functional properties in Formica decorative laminates. To prepare a decorative laminate, a melamine resin-impregnated decorative sheet is sandwiched between a melamine resin-treated protective overlay layer and a number of phenolic resin-treated support layers. The resulting combination provides the remarkable properties of the decorative appearance of the printed pattern protected by the hard, stain-resistant, and abrasion resistant surface provided by the melamine-formaldehyde resin.

## Miscellaneous Applications

Fiberglass insulation that is bonded with a phenolic resin is made more fire resistant by adding an amino resin. An amino resin adhesive may be used to bond a fire retardant to flammable draperies.

Amino resin adhesives may also be used to improve bonding between other materials. For example, tire cord is normally treated with a rubber latex to improve adhesion to the vulcanized rubber. The latex dip solution may also contain a resorcinol-formaldehyde resin or an amino resin to improve the bonding. Both urea and melamine resins are mentioned in patents, but melamine-formaldehyde is said to be most effective.

Regenerated cellulose film does not have good water resistance but may be made much more water resistant by coating it with a film of nitrocellulose or polyvinylidene chloride. The cellophane film is first passed through a dip tank containing about 1% of a melamine-formaldehyde acid colloid resin. This type of resin is called an *anchoring agent*. It improves the adhesion between the waterproofing coating and the cellophane film.

Urea-formaldehyde resin is also commonly used to bind the sand together to make the cores that are placed in molds for casting hollow metal shapes. The amino resin is mixed with the moist sand and formed into the desired shape. After drying and curing, the core is assembled into the mold. The sand core is stable enough to hold the molten metal to the desired shape until the metal solidifies. The continued heating of the sand core breaks down the resin so that the loose sand may be poured out by the time that the molding has cooled down and solidified to the desired shape.

A rapidly growing market for urea-formaldehyde adhesive resin is in use as a binder for the glass fiber mats used in the manufacture of shingles and built-up roofing. It is expected that this market will have an annual growth rate of 10% per year for the next few years.

## TOXICITY

*Urea* and *melamine* are considered nontoxic. Urea is used as a feed supplement for ruminant animals such as cattle and sheep. The rumen

microorganisms convert the urea to protein that can be used as food by the animal. Melamine has caused no ill effects in rats even when they are fed high concentrations. Fully cured amino plastics, such as urea-formaldehyde bottle caps and molded melamine-formaldehyde plastic dinnerware are also considered nontoxic.

*Formaldehyde* is a toxic gas and may be released from some amino-formaldehyde resins even after curing. This is true for urea-formaldehyde foam insulation and for urea-formaldehyde adhesives used in plywood and particle board. Formaldehyde can irritate the eyes, nose, and throat. In some cases an allergic reaction develops so that complete removal from formaldehyde vapors is required. Formaldehyde has also been found to cause cancer in laboratory animals. It is not uncommon for adhesives based on urea-formaldehyde resin to contain some additive to react with the formaldehyde that might be released in the curing reaction. Many countries have adopted restrictive standards limiting the amount of formaldehyde that may be released from particleboard that is used in the construction of residential housing. West Germany is reported to have one of the most stringent formaldehyde regulations.<sup>8,9</sup>

## AMINO RESIN PRODUCTION

American suppliers of amino resins include:

American Cyanamid Company, Chemicals Group.  
Borden, Inc., Chemical Division.  
Chembond Corporation.

Henkel Corporation.  
Monsanto Chemical Company.  
Monomer-Polymer and Dajac Labs. Inc.  
Reichhold Chemicals, Inc.  
T. R. America Chemicals, Inc.

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# Epoxy Resin Adhesives

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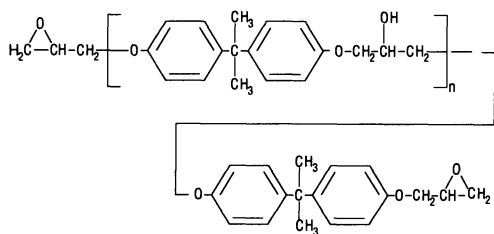
## INTRODUCTION

Structural adhesives based on epoxy resins were first introduced in 1950 and their use has grown steadily since. Epoxy resins are reactive with a number of different curing agents and yield a wide variety of products with different cure requirements and end-use performance. Epoxy resins cure with no evolution of byproducts, have low shrinkage and adhere to many different substrates. Although epoxy adhesives represent only a small part of the total adhesives market, they are unequalled in performance where high strength and endurance properties are critical.

## EPOXY RESINS USED IN ADHESIVES

### Bisphenol A Based Epoxy Resins

The most widely used epoxy resins are based on Bisphenol A and epichlorohydrin. The chemical structure is:



Bisphenol A epoxy resins are difunctional, with epoxide groups on the ends of the chain. As the molecular weight is increased, the resin retains its epoxide difunctionality while adding  $n$  repeating groups as shown above. The epoxide equivalent weight (EEW) is one-half of the molecular weight:

$$\text{Epoxide Equivalent Weight (EEW)} = \frac{\text{Molecular Weight}}{2}$$

Commercial liquid resins such as D.E.R. 331 (Dow), Epon 828 (Shell), Araldite 6010 (Ciba-Geigy), Epi-Rez 510 (Interez), and Epotuf 37-1410 (Reichhold) range in viscosity from 10,000 to 16,000 cps at 25°C and have an average  $n$  value of 0.15. Above  $n = 2$ , epoxy resins become nonsintering solids characterized by high molecular weights, high viscosities, and low weight percent epoxide contents. Fig. 1 shows various relationships which exist between the liquid and solid Bisphenol A based epoxy resins.

### Epoxy Novolac Resins

Epoxy novolac resins are produced by reacting a novolac resin with epichlorohydrin to obtain epoxy functionality. Unlike the Bisphenol A based resins, the epoxy novolac resins have an

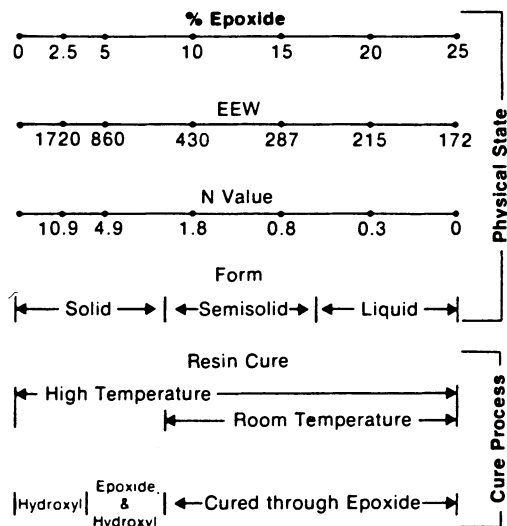
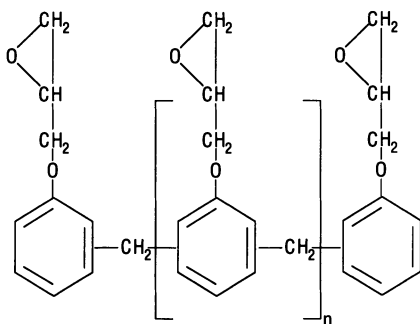


Fig. 1. Comparative physical and curing properties for liquid and solid Bis-A based resins.

epoxide group on each repeating unit as shown in the following structure:

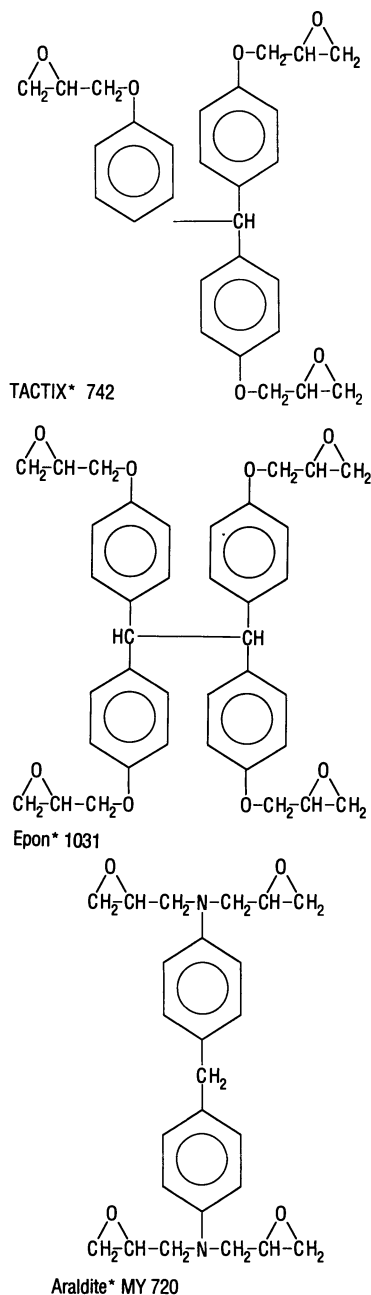


The increased functionality yields cured adhesives with higher crosslink densities resulting in higher temperature performance and increased chemical resistance. The functionality of commercially available, phenol based epoxy novolac resins varies from 2.3 to 6.0. Epoxy novolac resins can also be produced from substituted phenols like creosol and polyhydroxy phenols such as resorcinol. In the United States, Dow Chemical and Ciba-Geigy supply both phenol and cresol based epoxy novolac resins.

Epoxy novolac resins are normally used as modifiers for Bisphenol A based epoxy resins in adhesives. When used alone, the epoxy novolac resins tend to yield adhesives which are too brittle for most applications.

## High Performance Epoxy Resins

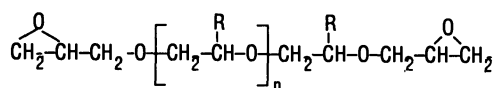
With the increased demand for high temperature and high humidity resistance, new resins have been developed which have higher epoxide and aromatic content. Three resins which fit the category are TACTIX 742 (Dow), Araldite MY 720 (Ciba-Geigy), and Epon 1031 (Shell). Their idealized structures are:



These high performance resins can be cross-linked with either an aromatic amine or a catalytic curing agent to induce epoxy-to-epoxy homopolymerization. High temperatures are required for these reactions to occur.

### Flexible Epoxy Resins

Long chain aliphatic epoxy resins based on a polyglycol or a vegetable oil fatty acid, when reacted with epichlorohydrin, are used as additives to flexibilize epoxy resin adhesives. They are not used alone because of their water sensitivity and overall lack of toughness. They serve as modifiers for Bisphenol A based epoxy resins. An idealized structure for flexible epoxy resins is shown below:



R - AN ORGANIC GROUP OR HYDROGEN

Examples of typical aliphatic epoxy resins based on polyol propylene glycol are D.E.R. 732 and D.E.R. 736 (Dow). Epi-Rez 505 (Interez) and Heloxy WC-85 (Wilmington Chemical) are typical flexible epoxy resins based on a vegetable oil fatty acid.

A compilation of commercial epoxy resins used in adhesives is shown in Table 1.

### CURING AGENTS USED IN ADHESIVES

The selection of an appropriate curing agent is as important as selecting the proper epoxy resin. The type of curing agent will determine the rate of reactivity, degree of exotherm, formulation viscosity, gel time, and the heat requirement during the cure cycle. In addition, application technique, pot life requirements, and the desired performance properties of the cured adhesive must be considered when selecting an epoxy curative. Curing agents determine the type of chemical bonds formed and the degree of crosslinking which occur with the epoxy resin. These factors, in turn, affect the chemical resistance, electrical and physical properties, and the heat resistance of the cured adhesive.

The types and number of curing agents available continues to grow rapidly. The chart in Table 2, taken from Dow Chemical's "General Guide to Formulating with Dow Epoxy Resins," summarizes the applications and advantages/disadvantages of different types of curing agents.

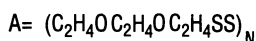
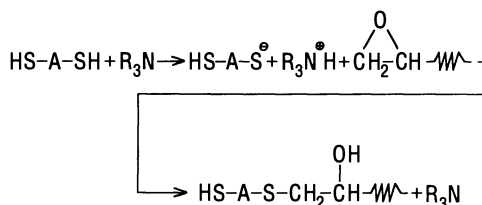
A brief description of various curing agents is provided to aid in the selection of an appropriate curing agent for a variety of adhesive applications.

### Polysulfides

An example of a typical polysulfide and its reaction sequence with an epoxide group is shown below:

#### REACTION SEQUENCE

#### MERCAPTAN



R = ALIPHATIC  
CYCLOALIPHATIC  
AROMATIC

The reaction between the terminal mercaptan and epoxide group proceeds very slowly at ambient temperature. However, the introduction of a basic material such as a tertiary amine greatly accelerates the cure. Polysulfides are typically used at ratios of 1:1 or less with epoxy resins, and can be used as co-curing agents with aliphatic amines. Stoichiometric quantities of aliphatic amine and 25 to 50 parts by weight of polysulfide will react with 100 parts by weight of epoxy resin.

Polysulfide/epoxy systems accelerated with tertiary amines exhibit good flexibility and tensile strength at ambient temperature. The aliphatic amine/polysulfide co-curing agent systems yield improved initial elevated tem-

**Table 1. Epoxy Resins Used in Adhesives.**

<i>Type</i>	<i>Viscosity @ 25°C, cps or Durrant's softening point</i>	<i>Epoxide Equivalent Weight</i>	<i>Commercial Products</i>	<i>Remarks</i>
Bisphenol A resins	4000–6500	172–180	D.E.R. 332 (Dow)	Virtually pure diglycidyl ether of Bisphenol A
low viscosity			Epon 825 (Shell); Araldite GY 6004 (Ciba Geigy); Epo-Tuf 37-15 (Reichhold)	
medium viscosity	7000–10,000	176–190	D.E.R. 330, D.E.R. 383, Araldite GY 6008, Epon 826, Epi-Rez 509 (Interez)	Undiluted resins with viscosity lower than standard resins.
standard liquid	11,000–14,000	182–195	D.E.R. 331, Araldite GY 6010, Epon 828, Epi-Rez 510, Epo-Tuf 37-140	Standard undiluted epoxy resins
high viscosity	16,000–25,000	200–250	D.E.R. 317, D.E.R. 337, Araldite GY 6020, Epon 834, Epo-Tuf 37-141	
solid	75–85°C, Durrant's softening points	500–575	D.E.R. 661, Epon 1001, Epi-Rez 520°C, Epo-Tuf 37-001, Araldite GT 7071	Low melting solid resin
Epoxy novolac resins	1100–1700 @ 52°C	172–179	D.E.N. 431	Phenolic novolac
	20,000–50,000 @ 52°C	176–181	D.E.N. 438, Araldite EPN 1138, D.E.N. 444	Phenolic novolac
Epoxy cresol novolac resins	175–350 @ 150°C	180–220	Quatrex 3310 (Dow)	High-purity electronic grades
	350–700 @ 150°C	180–230	Quatrex 3410	
	700–1300 @ 150°C	190–230	Quatrex 3710	
	73°C SP	215–230	Araldite 1273	
	80°C SP	235 Max.	Araldite 1280	
	99°C SP	220–245	Araldite 1299	

perature performance. Both systems, however, lose some flexibility on aging.

### Amines

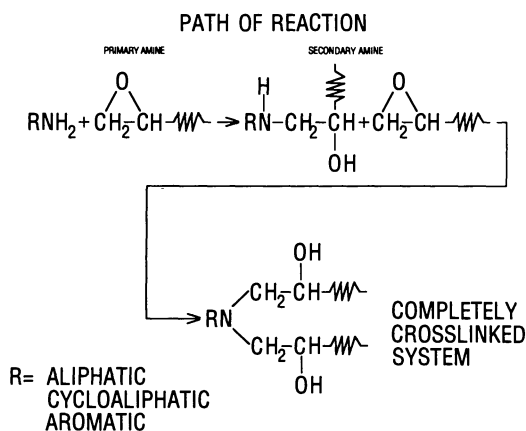
The functionality of an amine is determined by the number of amine hydrogens present on the

molecule. A primary amine group (nitrogen with two hydrogens bound to it) will react with two epoxide groups. A secondary amine group (nitrogen with only one hydrogen bound to it) will react with one epoxide group. A tertiary amine group (nitrogen with no hydrogens

**Table 2. Applications and Characteristics of Epoxy Curing Agents.**

Type	Advantage	Disadvantage	Application
Polysulfides	Moisture insensitive, quick set time, flexible	Odor, poor elevated temperature performance	Adhesives, sealants
Aliphatic amines	Convenience, room temperature cure, low viscosity, low formulation cost	Critical mix ratios, strong skin irritant, high vapor pressure, blushes	Civil engineering, adhesives, grouts, casting and electrical encapsulation
Polyamides	Convenience, room temperature cure, low toxicity, good flexibility or resilience, good toughness	Higher formulation cost, high viscosity, low heat resistance, low vapor pressure	Civil engineering, adhesives, grouts, castings, coatings
Amidoamines	Reduced volatility, convenient mix ratios, good toughness	Poor elevated temperature performance, some incompatibility with epoxy resin	Construction adhesives, concrete bonding, troweling compounds
Aromatic amines	Moderate heat resistance, good chemical resistance	Solids at room temperature, long elevated-temperature cure schedules	Filament wound pipe, electrical encapsulation, adhesives
Dicyandiamide	Latent cure, good elevated temperature properties, good electrical properties	Long elevated-temperature cure, insoluble in resin	Powder coatings, electrical laminates, one-component adhesives
Catalytic	Extremely long pot life, high heat resistance	Long elevated-temperature cure schedules, poor moisture resistance	Adhesives, electrical, encapsulation, powder coatings, electric laminates
Anhydrides	Good heat resistance, good chemical resistance	Long elevated-temperature cure schedules, critical mix ratios	Filament wound pipe, electrical encapsulation and adhesives
Melamine/formaldehyde	Good hardness and flexibility, one-package stability, solvent-free systems	Elevated temperature cure	Waterborne coatings, container and deco finishes
Urea/formaldehyde	Good film color, one-package stability, good intercoat adhesion	Elevated temperature cure	Fast bake enamels, primers and topcoats
Phenol/formaldehyde	Good elevated temperature properties, good chemical resistance, good hardness and flexibility	Solid, poor weatherability	Powder coatings, molding compounds

bound to it) will not react readily with an epoxide group, but will act as a catalyst to accelerate epoxy reactions. A typical amine reaction sequence is shown below:



Theoretically, the hydroxyl groups generated in the above reaction sequence are capable of reacting with other epoxide groups, thus forming an ether linkage. This reaction can be catalyzed by tertiary amines.

## Aliphatic Amines

The liquid aliphatic polyamines and their adducts are convenient to handle and give good cured resin physical properties, including excellent chemical and solvent resistance. Mix ratios are critical for optimum performance. Aliphatic amines offer fast curing at ambient temperatures. Pot life is short and high exotherm in thick sections or large masses can lead to thermal decomposition. Good long-term retention of properties is possible at temperatures



up to 100°C (212°F). Short-term exposure to higher temperatures can be tolerated. Epoxy resin formulations containing aliphatic amines will blush under very humid conditions.

Adducted aliphatic polyamines such as D. E. H. 52 (Dow) epoxy hardener and D. E. H. 58 (Dow) epoxy hardener offer the advantages of lower vapor pressure, reduced tendency to blush, and less critical mix ratios.

### Cycloaliphatic Amines

When compared to aliphatic polyamines, cycloaliphatic amines produce cured resins having improved thermal resistance and toughness. Glass transition temperatures approach those of aromatic amines while percent elongation can be doubled. Because cycloaliphatic amines are less reactive than aliphatic polyamines, their use results in a longer pot life and in the ability to cast larger masses.

### Aromatic Amines

Aromatic amines are solids at room temperature. These hardeners are routinely melted at elevated temperatures and blended with warmed resin. Eutectic mixtures of metaphenylene diamine and methylene dianiline exhibit a depressed melting point resulting in an aromatic hardener that remains a liquid over short periods of time. The pot life is considerably longer than that achieved with aliphatic polyamines. Elevated temperature cures are required to develop optimum properties which are maintained at temperatures up to 150°C (300°F). Aromatic amines have improved chemical and thermal resistance when compared to aliphatic polyamines.

### Polyamides

The most commonly used polyamides are the condensation products of dimerized fatty acids and aliphatic amines such as diethylene triamine. A range of molecular weights are available making polyamide curing agents versatile in a variety of adhesive applications. The polyamides react with epoxide groups through the unreacted amine functional groups in the polyamide backbone. As a result of their relatively large molecular weight, the ratio of

polyamide to epoxy is more forgiving (less critical) than with low molecular weight polyamines. Polyamides also offer the advantages of curing without blushing, and improved adhesion. However, they are much darker in color than polyamines.

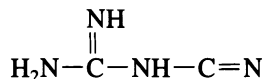
The various molecular weight polyamides exhibit different degrees of compatibility with epoxy resins. To ensure optimum properties, the polyamide/epoxy mixture must be allowed to react partially before being used. The partial reaction assures compatibility and is known as the induction period. Because polyamides have a long pot life, the induction time does not significantly shorten the usable time of the system.

Polyamide-cured epoxides lose structural strength rapidly with increasing temperature. This limits their use to adhesive applications which will not be subjected to temperatures above 65°C (148°F).

### Amidoamines

Amidoamines are derivatives of monobasic carboxylic acids (such as ricinoleic acid) and an aliphatic polyamine. Like the polyamides, amidoamines can be used over a range of additive levels to enhance a specific property. The reactivity of amidoamines with epoxies is similar to that of polyamides. However, amidoamines offer several advantages over aliphatic amines and polyamines: more convenient mix ratios, increased flexibility, better moisture resistance than aliphatic polyamines, and lower viscosity and color than polyamides.

### Dicyandiamide

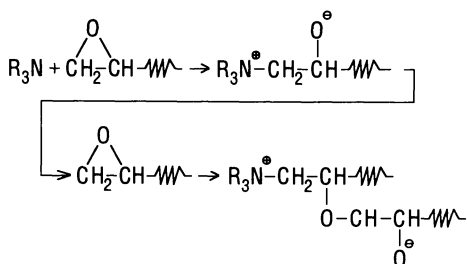


Dicyandiamide (Dicy) is a solid curing agent which, when ball milled into liquid epoxy resins, provides one-package stability for up to six months at ambient temperature. Cures occur with heating to 150°C (300°F). A tertiary amine accelerator is necessary for rapid cures. Dicy offers the advantage of being latent (reacts with epoxy resins upon heating, and stops reacting when the heat is removed). This par-

tially cured or "B-staged" state is ideal for prepregs for supported film adhesives. Typically, dicyandiamide is used at levels of 5-7 parts per 100 parts liquid epoxy resin, and at levels of 3-4 parts per 100 parts solid epoxy resin.

## Catalytic Curing Agents

Catalytic curing agents are a group of compounds which promote epoxy to epoxy reactions without being consumed in the process. A typical epoxy homopolymerization using a tertiary amine is shown below:



Stable, one-package systems can be developed with many catalytic curing agents such as the boron trifluoride complexes. Tertiary amines and amine salts have pot lives generally ranging from 2 to 24 hours. The latent catalysts are activated by heat and cause a disassociation of the active catalyst from the blocking group.

The amount of catalyst used may vary from 2 to 10 parts per 100 parts resin. To determine the best ratio of catalyst to resin, several different catalyst levels should be evaluated to determine which level provides maximum properties. Several common catalytic curing agents are benzyldimethylamine (BDMA), boron trifluoride monoethylamine ( $\text{BF}_3 \cdot \text{MEA}$ ), and 2-methylimidazole (2-MI).

## Anhydrides

Liquid and solid anhydrides are used extensively to cure epoxy resins. The reactivity of some anhydrides with epoxies is slow, therefore an accelerator, usually a tertiary amine, is often used at 0.5–3% to speed gel time and cure. The optimum amount is usually critical, and is dependent on the anhydride, the resin used, and cure schedules. The amount of accelerator above or below the “optimum” concentration can result in reduced high

temperature performance. The optimum concentration of accelerator should be determined experimentally. Eutectic mixtures to depress melting points may be prepared.

The reaction of anhydrides with epoxide groups is complex, with several competing reactions capable of taking place. The three most important are:

1. The opening of the anhydride ring with an alcoholic hydroxyl to form the monoester.
2. Subsequent to the opening of the ring, the nascent carboxylic groups react with the epoxide to give an ester linkage.
3. The epoxide groups react with nascent or existing hydroxyl groups, catalyzed by the acid, producing an ether linkage.

At low elevated temperature cures, the ether and ester reactions take place at about the same frequency. At higher temperatures, the ester linkage occurs more frequently and this probably accounts for the reduced elevated temperature performance of systems gelled at initially high temperatures. Because reaction 3 can take place independently in the acid medium, the ratio of anhydride to epoxy is less critical than with an amine. It can vary from 0.5 to 0.9 equivalents of epoxy and is determined experimentally to achieve desired properties.

Compared to aliphatic amine cures, the pot life of epoxy-anhydride formulations is usually long and exotherm is low. Elevated temperature cures (up to 200°C) are necessary and long post-cures are required to develop ultimate properties. Electrical and physical strength properties are good over a wide temperature range. Compared to amine-cured systems, anhydride-cured systems offer better chemical resistance to aqueous acids and less chemical resistance to some reagents.

## SUMMARY

The most commonly used curing agents for ambient cured adhesives are polyamides, aliphatic amines, cycloaliphatic amines and aminoamines. The choice of hardener is dependent on the performance requirements of the adhesive. For high performance, high temperature

**Table 3. Curing Agents for Epoxy Resins Adhesives.**

<i>Curing agent</i>	<i>Recommended Parts/100 parts Liquid resin</i>	<i>Curing Temperature °C</i>	<i>Curing agent Suppliers and Trade Names</i>
<b>Aliphatic amines</b>			
diethylene triamine (DETA)	8-10	R.T.-150	D.E.H. (The Dow Chemical Company)
triethylene tetramine (TETA)	10-13	R.T.-150	Amicure (Pacific Anchor Chemical Co.)
Aminoethyl piperazine (AEP)	20-23	R.T.-150	Epo-Tuf (Reichhold Chemical)
<b>Aromatic amines</b>			
methylene dianiline	51-55	175 (2 hr)	Curithane (Dow)
4,4-diaminodiphenyl sulfone	30-34	175 (2 hr)	
MDA/MPDA eutectics			Amicure (Air Products and Chemicals, Inc.) Ancamine (Pacific Anchor) Epon (Shell Chemical Company)
<b>Cycloaliphatic amines</b>			
wide variety of modified products from major curing agent suppliers		R.T.-150	Amicure (Air Products) Ancamine (Pacific Anchor) Azamine (SHEREX) Epo-Tuf (Reichhold) Versamine (Henkel Corporation)
<b>Polyamides</b>			
wide variety of polyamide curing agent with range of molecular weights.		R.T. to 2 hr @ 100	All major curing agent suppliers listed above offer Polyamide curing agents.
<b>Heat activated curing agents and catalysts</b>			
benzyl dimethylamine (BDMA)	2-4	150 (2 hr)	Air Products and Chemical, Inc.
dicyandiamide (DICY)	2-4	150 (2 hr)	Pacific Anchor Chemical Corp.
boron trifluoride amine complexes	2-4	150 (2 hr)	Allied Chemical, Ciba-Geigy, Sylvachem (Sub. of Arizona Chem.)

resistant adhesives, the aromatic amines, dicyandiamide, and catalytic curing agents are used.

Table 3 contains a list of curing agents used in adhesives and their manufacturers.

## DILUENTS

Diluents are used in epoxy adhesive formulations to reduce viscosity and to allow the use

of large amounts of filler. Both reactive and nonreactive diluents are used. Reactive diluents are low viscosity mono or difunctional epoxy materials. Table 4 lists reactive epoxy diluents in descending order of viscosity.

Nonreactive diluents are not as widely used as reactive diluents in epoxy resin adhesives because they decrease the cured properties more than a reactive diluent and have a tendency to migrate to the surface of the adhesive bond. The

**Table 4. Reactive Diluents For Epoxy Adhesives.**

<i>Diluents</i>	<i>cps at 25°C</i>
Butyl glycidyl ether	2 max.
2-Ethylhexyl glycidyl ether	1-4
<i>t</i> -Butyl glycidyl ether	2-5
Phenyl glycidyl ether	4-7
<i>o</i> -Cresyl glycidyl ether	2-10
C <sub>12</sub> -C <sub>14</sub> alkyl glycidyl ether	6-10
Diglycidyl ether of 1,4 butanediol	14-18

advantage of non-reactive diluents is their lower cost compared to reactive diluents. Table 5 contains a list of non-reactive diluents used in epoxy resin adhesives.

### FILLERS

Fillers are incorporated in epoxy resin adhesive formulations to enhance or obtain specific desired properties and to reduce cost. The amount and type of filler used are determined by the specific properties desired.

The amount of filler by weight that can be incorporated into an epoxy adhesive will depend on the filler's particle size, shape, density and oil absorption properties. Porous, high-oil-absorption fillers such as diatomaceous silicas and chopped glass will greatly increase the viscosity of an epoxy adhesive with low filler loadings of 20-50 parts per hundred resin (phr). Oil absorbent, granular fillers of medium weight, such as powdered aluminum and alumina, may be used at loadings up to 200 phr. Nonporous, lower oil absorbent fillers like aluminum oxide, silica, and calcium carbonates can be incorporated at levels of 700-800 phr without producing an unusable formulation.

Filler loadings can be increased by using a diluent, although diluents will usually detract from the physical properties of the cured ad-

hesive. Organotitanates, zircoaluminates, or silanes can be added to formulations to improve filler wetting, enabling higher filler loadings without increasing the viscosity.

Table 6 contains a compilation of the effect of various fillers on the physical properties of cured epoxy resin systems.

### ELASTOMERIC MODIFIERS

Elastomeric modifiers are used to increase the peel strength (toughness) of epoxy resin adhesives. The most commonly used elastomeric materials are functionally terminated polybutadiene resins made by the B.F. Goodrich Company, Chemical Group under the trade name of Hycar Reactive Liquid Polymers. Initially, carboxyl-terminated butadiene acrylonitrile (CTBN) resins were introduced; the carboxyl terminated materials are usually adducted with the epoxy resin to improve compatibility and to increase the toughness.

The latest addition to reactive liquid polymers are amine-terminated butadiene acrylonitrile rubbers. These amine-terminated polymers are added to the hardener side of two-component epoxy resin adhesives. The carboxyl or amine terminated polymers may be used at relatively low concentrations, about 3-30 parts of rubber per 100 parts resin, to produce toughened epoxy resins. These toughened epoxy resins provide greatly improved impact resistance and fracture surface energies with little loss of modulus and hot strength. Higher concentrations of rubber (30-100 phr) produce epoxy adhesives with large increases in tensile elongation, and resistance to thermal shock, but with lower room temperature strength, stiffness, and hot strength.

### TYPICAL ADHESIVE FORMULATIONS

The following are examples of typical epoxy resin adhesive systems. One of the advantages of epoxy based adhesives is the wide choice of available curing agents, allowing the formulator to produce adhesives with either fast ambient cures, high temperature cures, or one package systems with extended shelf life.

**Table 5. Non-reactive Diluents For Epoxy Adhesives.**

Nonyl phenol
Diocetyl phthalate
Dibutyl phthalate
Furfuryl alcohol
Pine oil
Coal tar

**Table 6. Effects of Fillers on Properties of Cured Epoxy Systems.<sup>a</sup>**

	<i>Improved Thermal Conductivity</i>	<i>Improved Machina- bility</i>	<i>Improved Abrasion Resistance</i>	<i>Im- proved Impact Strength</i>	<i>Improved Electrical Conductivity</i>	<i>Improved Thixotrop Response</i>
Additives	Calcium car- bonate, calcium silicate, powdered aluminum, or copper	Alumina, flint pow- der, carbo- rundum, silica, or molybde- num disul- fide	Chopped glass	Mica, silica, pow- dered or flaked glass	Metallic fill- ers, or al- umina	Colloidal silica, Benton- ite clay
Cost	D	D	N	D	D	I
Exotherm	D	D	D	D	D	D
Thermal con- ductivity	I	I	I	I	I	D
Heat deflection temp.	I	I	I	I	I	N
Machinability	I	D	D	D	I	I
Abrasion resis- tance	N	I	I	I	D	D
Impact strength	D	D	I	D	D	N
Tensile strength	D	N	I	D	N	N
Flexural strength	D	N	I	D	N	N
Compressive strength	D	N	I	D	N	N
Dielectric con- stant	I	I	I	I	I	N
Thixotropy	N	N	N	N	N	I

<sup>a</sup>D, decrease; I, increase; N, essentially no effect.**Epoxy Concrete Adhesive****Part A**

Thiokol LP-3	100
Hydrite Clay 121	140
Trimethylaminomethyl phenol	20
Toluene	65

**Part B**

D.E.R. 331	200
Hydrite Clay 121	105
Toluene	5

**Room Temperature Cure General Use  
Adhesive****Part A**

Liquid Epoxy Resin (EEW = 190)	70
D.E.R. 732 Aliphatic Epoxy Resin	30
Alumina T-60	50

**Part B**

Triethylene Tetramine	13
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The following test results are reported by Thiokol when the formulation is used to bond new to old concrete after 7 days aging at 80°F:

Tensile strength, psi	450
Flexural strength, psi	345
Compressive shear strength, psi	4350

All failures were in the concrete.

**Tensile Shear Strengths (psi)**

Substrate	Cured 7 Days @ 75°F	Cured 2 hrs @ 200°F
Aluminum, 16 gauge	1150	1600
Stainless steel, 16 gauge	1400	1730

General Purpose Adhesive  
for Temperatures Up to 150°C

*Part A*

D.E.N. 438	90
D.E.R. 736	10
Atomized Aluminum Powder	40

*Part B*

Cycloaliphatic Amine	28
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Supported Epoxy Film Adhesive

D.E.R. 331	100
D.E.N. 438-A85	100
Solvent	until desired viscosity reached
Dicyandiamide	16
Benzyl dimethyl amine (BDMA)	2-4

- Mix resins and solvent. Ball mill curing agent into varnish.
- Varnish is then B-staged on desired film backing (e.g., glass cloth or graphite) and heat cure in place.

Unsupported Film Adhesive  
Cast From Solvent Solution

D.E.R. 684 EK 40	212
D.E.N. 438 EK 85	37.5
Dicyandiamide	12
Benzyl dimethylamine	1.0
Solvent removal	1 hr @ 180°F
Dry film thickness	0.002
Cure schedule	1 hr @ 175°C
Pressure	120 psi

## COMPLEMENTARY TECHNOLOGIES

New technologies which will impact the growth of adhesives in assembly line applications are robotics and induction curing.

### Robotics

The use of robots is fast growing in prominence in the field of material dispensing, especially in the application of adhesive and sealants. Companies who have installed robots to dispense adhesives or sealants have realized rapid pay-back of their capital investment because of the following benefits:

- More uniform application of the adhesive bead results in higher quality finished products.
- Decreased adhesive or sealant material costs. Material use can be decreased by as much as 30%.
- Better utilization of people and machinery plus increased process flexibility.
- Improved working environment because the operator is not in constant contact with volatile components released from the adhesive or sealant.

Industries leading in the use of robotics are the appliance, automotive, and furniture manufacturing.

### Induction Curing

The expanded use of adhesives for bonding advanced composites and metallic structures together could be restricted by the need for jigs or spot welding to hold the components together until the adhesive cures to the extent of providing structural strength. Reaching this point can require heating to high temperatures (300–400°F) the part being produced and the jiggling equipment. Induction heating techniques can eliminate these needs by providing heat directly to the bond line and/or adherends without heating the entire structure, supports and fixtures of a bonding assembly. Bonding times for specimens can be cut by a factor of 10–100 compared to standard press bonding.

Induction heating is produced when a current passing through a conductive coil produces a magnetic flux inside and around the coil. When a mass of conducting metal (susceptor) is moved into the magnetic field or is subjected to a changing flux, induced currents called *eddy currents* circulate in the susceptor producing heat. Susceptors can be incorporated into the adhesive bond line by using magnetic iron oxide, iron filings or carbon as a filler in the adhesive formulation or imbedding a steel screen or perforated steel foil in the adhesive bond line. The heat produced will cause the epoxy adhesive to cure. Ideal induction cure adhesives will have a broad cure temperature of 275–425°F and no adverse affect by overheating.

## APPLICATIONS AND SUMMARY

Adhesives based on epoxy resins can be formulated to bond to a variety of substrates and perform over a broad range of conditions. They are used in one- or two-component pastes or films which are curable under ambient or elevated temperatures. Film adhesives, most commonly formulated with Bisphenol A and/or novolac epoxy resins and latent curing agents and impregnated on glass cloth or other mediums, can be stored for prolonged time periods prior to cutting and heat curing.

When compared to other polymeric adhesives, epoxy adhesives have the following advantages:

- Excellent tensile shear strength.
- Good moisture, humidity, chemical, and high temperature resistance.
- No evolution of volatiles and low shrinkage during cure.
- Good surface wetting ability.
- Low creep under prolonged stress conditions.

Adhesives based on epoxy resins find use in the consumer, furniture, construction, automotive, aircraft/aerospace, electrical/electronic and industrial tool maintenance industries where they provide both protective and load bearing properties.

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# Polyurethane- and Isocyanate-Based Adhesives

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The most important polyurethane adhesive components continue to be toluene diisocyanate (TDI) (I)\*, diphenylmethane-4,4'-diisocyanate (MDI) (VIII), polymethylene polyphenyl isocyanate (PAPI) (XV), and triphenylmethane triisocyanate (Desmodur R) (III) together with various polyester and polyether glycols. One review points out that polyester based polyurethanes have emerged as the forerunner over polyether systems because of their inherently higher cohesive and adhesive properties.<sup>54</sup> Nevertheless, poly(ether-urethane) adhesive compositions unquestionably have useful adhesive properties.<sup>78</sup>

The use of polyurethane- and isocyanate-based adhesives in the United States is estimated to have grown from a level of less than 100,000 lb in 1960 to 10–12 million pounds in 1972.<sup>1</sup> Although substantial, this growth was considered by many to be unimpressive for the time span involved.<sup>2,3</sup> However, existing as well as new high-performance polyurethane adhesive systems for specialized industrial applications generated a 97 million dollar business by 1981, distributed as follows:<sup>81</sup>

## 1981 Polyurethane Adhesives Market

Market	Sales, \$MM	Applications
Textile	20	Fabric tie-coats, flocking

Market	Sales, \$MM	Applications
Food packaging	20	Film and foil lamination
Footwear	15	Vinyl-to-leather and canvas
Consumer	3.5	Do-it-yourself products
Construction	10	Film lamination for wall panel, outdoor carpet
Furniture	20	Lamination to particle board
Automotive	8	SMC to SMC, interior trim
Aircraft	0.5	Interior plastics
Total	97	

Their multiple use-forms (e.g., in *in situ*-reacting, neat, liquid systems; solutions; aqueous dispersions; films; webs; powders) and other valuable attributes (e.g., adhesion to a variety of substrates; vibration-damping bonds;<sup>4,13</sup> gasoline, oil, and solvent resistance; etc.) continue to make polyurethane- and isocyanate-based adhesives the materials of choice in many adhesive applications.

The practical basis for polyurethane adhesive use is abundantly evident, for example, in fast sole-to-upper bonding in footwear; strong, flexible adhesion with high pigment loadings in magnetic oxide binders for magnetic tape; dis-

\*Roman numerals refer to structural formulas at end of chapter.



similar material bonding in film laminates; strong, flexible, solvent-resistant urethane foam-fabric bonds in apparel; toughness in abrasion devices; application ease in electrical systems; etc.

A special polyester glycol type, polycaprolactone glycol (XXVI), has become well established as a polyurethane adhesive component.<sup>54</sup> And still another macroglycol type, polybutadiene glycol (Poly BD glycol) (XXVII) has gained use in polyurethane adhesive systems.<sup>79</sup>

Thermoplastic polyurethanes continue to hold the imposing inroads they have made in adhesive applications. And ecological considerations direct growing attention to nonpolluting urethane adhesive forms, e.g., powders, films, aqueous dispersions, and 100% solids reactive systems.

This chapter builds on an earlier one.<sup>5</sup> It includes what are considered to be some of the more important developments and considerations in the field of polyurethane- and isocyanate-based adhesives. In addition, it includes information from other areas of polyurethane technology and chemistry such as polymer stability and stabilization, since these are relevant to adhesive applications. The reader may also wish to consult other references<sup>2,6a,7,8,82a,b</sup>, which review information on the present subject.

## DEVELOPMENT OF THE USE OF POLYURETHANES AND ISOCYANATES IN ADHESIVES

Allied interrogation teams, who were assigned the task of studying the state of development of the German plastics and rubber industries at the end of World War II, reported substantial accomplishments in the preparation and use of isocyanates in Germany during the war. Not among the least of these was their use in adhesive systems.

A translation of a portion of a German technical paper appearing in a CIOS Report,<sup>9</sup> the section later appearing in essence in a German scientific publication<sup>10</sup> and referred to in a monograph on polyurethanes<sup>11</sup> indicates that the exceptional and useful adhesive properties of the isocyanates became apparent to investigators of the I. G. Farbenindustrie, A. G., laboratories about 1940.

In the course of attempting to vulcanize hydroxylated buna (polybutadiene) rubbers and hydroxyl-bearing buna copolymer rubbers with diisocyanates (to replace a sulfur cure) they discovered that Buna-S and natural rubber both undergo distinct vulcanization effects with diisocyanates. Of greater importance to the present subject was their observation that such stocks adhered strongly to the metal parts of the vulcanization press after the cure. This effect was studied more thoroughly in cooperation with the Central Rubber Laboratory of I. G. Farbenindustrie. Such studies led to "the long-sought adhesive for applying buna to various supports."

Heat-stable bonds of normal buna-sulfur mixtures to iron, light metals, porcelain, etc., with strengths up to 1138 psi (stock failure) were realized using toluene diisocyanate (I) and hexamethylene diisocyanate (II). Still, some problems in the use of isocyanates in adhesive systems were encountered. Thus, "Desmodur R (III) had shown outstanding adhesion in bonding rubber tank treads to steel. It still gave erratic performance, however, and needed further development."<sup>12</sup> These studies apparently represented the beginning of the diverse application of isocyanates in adhesive systems in Germany.

One could easily conclude that the above development was related to the use of diisocyanates as coupling agents in the preparation of polyurethane plastics and elastomers, whose intense study was in progress in Germany at about the same time. At any rate, German exploitation of di- and polyisocyanates ("Desmodurs") in adhesive systems centered for the most part on their use in admixture with reactive, low molecular weight, hydroxyl-terminated polyesters ("Desmophens"). Combinations of certain "Desmodurs" and "Desmophens" comprised the "Polystal" line of adhesives. Concerning these it is stated: "The Desmodur-Desmophen systems were reported to give some of the best adhesives yet developed. They were said to stick "anything to anything." The advantages were: curing at low temperatures, good bond strength, versatility, good water resistance, and good low temperature flexibility."<sup>12</sup>

In somewhat greater detail: "the varieties sold in small amounts as "Polystal" were tough, resistant combinations of a flexible alkyd such as "Desmophen 1200" (IV) with an isocyanate such as "Desmodur TH" (V) and an auxiliary such as an amine or anything which would change the pH. Cures were immensely speeded by acid, alkali, or a little triethylamine. For a tough, cold-curing wood adhesive, to be used where vibration was bad, they proposed 40 parts of a 70% ethyl acetate solution of "Desmophen 900" (VI) and 100 parts of a 75% ethyl acetate solution of "Desmodur TH" (V)."<sup>9,12</sup>

German enthusiasm for isocyanate-based adhesive systems proves to have been justified. Buist and Naunton were later to conclude the following concerning rubber-metal adhesion: "On the whole, when tested by a discriminating method (by impact) isocyanate-based cements give higher strength than do other cements. The bonds are fast to heat and solvents, and are better able to withstand continued fatigue. The polyisocyanates suffer from the disadvantage that they are highly reactive chemicals and must be treated as such by avoiding their contact with moisture and the skin. For many uses, the better results justify the extra care necessary in using them."<sup>13</sup>

## REASONS FOR THE EFFECTIVENESS OF POLYURETHANE AND ISOCYANATE-BASED ADHESIVES

The effectiveness of isocyanate-based adhesives involves a combination of several features which are characteristic of the materials:

1. Isocyanates react readily with a variety of other functional groups.
2. Di- and polyisocyanates can undergo self polymerization to form three dimensional resins in situ.<sup>9,10</sup>
3. Isocyanates are quite soluble in many organic substances, and due to their small molecular size readily permeate insoluble porous structures.<sup>10</sup>
4. The reaction of di- and polyisocyanates with hydroxyl-bearing polyesters and polyethers, co-reactants in many isocyanate adhesive applications, produces the strong, polar, hydrogen-bonded, flexible

polyurethanes which wet, intimately contact, and show strong attraction for a variety of surfaces.

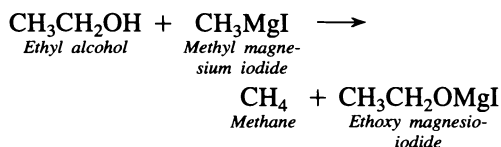
5. Isocyanates provide elastomer-metal bonds whose favorable gradation in physical properties between elastomer and metal affords superior fatigue life.<sup>13</sup>
6. Isocyanates "react even with hydrated oxide layers on metal surfaces, thus producing a clean surface, and therein, most probably allowing the urea groups of the adhesive to form chemical bonds with the residual valencies of the metal lattice."<sup>9,10</sup>

Let's look more closely at the foregoing features of isocyanates which contribute to their effectiveness as adhesives.

1. Reaction of isocyanates with other functional groups. In considering the likelihood of adhering two objects with an adhesive, one is more inclined to expect strong adhesion if the development of chemical bonds linking adherend to adhesive is a possibility. The ready reaction of the isocyanate group with a large number of other functional groups would, on this basis, favor the success of isocyanate-based compositions as adhesives.

Organic isocyanates tend to react, in many cases quite readily, with substances containing active hydrogen atoms, that is, with hydrogen atoms reactive enough to be replaced in their compounds by alkali metals<sup>10</sup> or by the Zerevitinoff reagent, methyl magnesium iodide.<sup>14</sup>

In the case of alcohols, for example ethyl alcohol, the hydrogen on the oxygen atom is an active hydrogen atom:

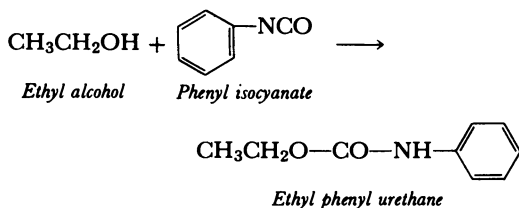


Functional groups containing active hydrogen atoms and, therefore, the ability to react with isocyanates, include: —OH (hydroxyl), —SH (sulfhydryl), —NH— (imino) —NH<sub>2</sub> (amino), —NHR (substituted amino), —NHCO—O— (carbamate), —NHCONH— (carbamide), —CO<sub>2</sub>H (carboxyl), —CONH<sub>2</sub> (carbonamide), —CONHR (substituted car-

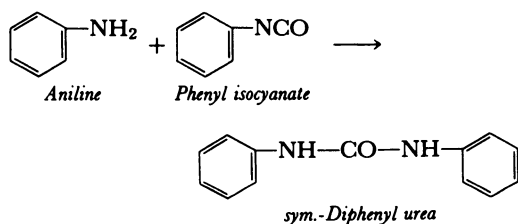
bonamide),  $-\text{CSNH}_2$  (thioamide),  $-\text{SO}_2\text{OH}$  (sulfonic), etc.

The reaction of isocyanates with some of these groups is illustrated below. For simplicity's sake, monoisocyanates are used in the equations to illustrate the chemistry. In actual adhesive applications, di- or polyisocyanates are used; therefore, the reader must realize that the reactions shown below occur in more than one position and concurrently in each isocyanate molecule.

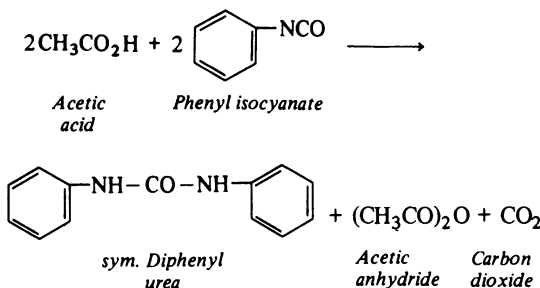
For example, isocyanates react with alcohols to produce urethanes (carbamates):



with amines to produce substituted ureas (carb-  
mides):



with carboxyl groups to produce substituted ureas, acid anhydrides, and carbon dioxide:



Aliphatic isocyanates yield substituted amides and carbon dioxide on reaction with carboxylic acids.

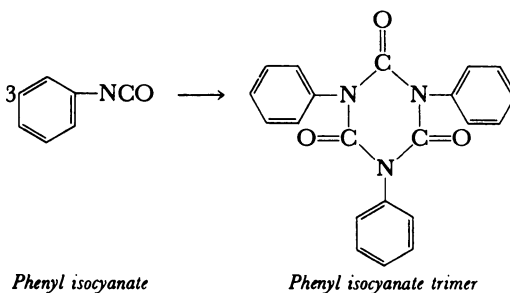
For some time the hydroxyl groups of raw cellulose (but not of its derivatives such as nitro, sec. acetyl, ethyl, benzyl, etc.) were considered to probably not react with isocyanate.<sup>10</sup> But this reaction has also been achieved.<sup>80</sup>

A quantitative indication of the readiness with which isocyanates react with certain active hydrogen groups is provided by Morton, Diesz, and Ohta.<sup>15,6b</sup> They found phenyl isocyanate to react with the following compounds at the indicated rates at 80°C in dioxane solution:

Active Hydrogen Compound	$K \times 10^4$ 1/Mole Sec	Relative Rate
<i>n</i> -Butyl phenyl carbamate	$0.02 \pm 0.02$	1
<i>n</i> -Butyranilide	$0.28 \pm 0.05$	14
Diphenyl urea	$1.48 \pm 0.06$	74
<i>n</i> -Butyric acid	$1.56 \pm 0.33$	78
Water	5.89 <sup>a</sup>	295 <sup>a</sup>
<i>n</i> -Butanol	27.5 <sup>a</sup>	1375 <sup>a</sup>

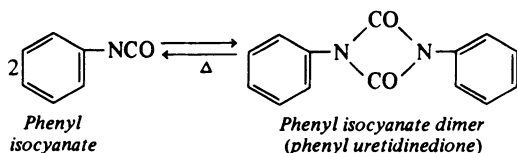
<sup>a</sup> Calculated from rate data obtained at lower temperatures.

2. Reaction with other isocyanate groups. Aromatic and aliphatic isocyanates can undergo self-reaction to form stable resinous trimer structures. The reaction is catalyzed by many materials including calcium acetate, potassium acetate, sodium formate, sodium carbonate, sodium methoxide, triethylamine, oxalic acid, sodium benzoate in dimethyl formamide, and a large number of soluble metal compounds of iron, sodium, potassium, magnesium, mercury, nickel, copper, zinc, aluminum, tin, vanadium, titanium, and chromium, titanium tetrabutylate, oxygen, and Friedel-Crafts type catalysts.<sup>6b</sup> Strong heating can also promote this change, which can be represented in the case of phenyl isocyanate as follows:



Some isocyanates also react with themselves to form thermally reversible dimer structures, the so-called uretidinediones. Such self reaction is apparently confined to aromatic

isocyanates<sup>6b</sup> and is illustrated with phenyl isocyanate:



The dimerization reaction is catalyzed vigorously by trialkyl phosphines and less by tertiary amines such as pyridine.

3. Solubility characteristics. Bayer<sup>9,10</sup> noted the excellent solubility of the isocyanates in practically every organic substance, and their small molecular size, which allows ready diffusion. These characteristics promote adhesion by allowing the isocyanates to penetrate the adherend. There they may undergo the foregoing multiple reactions all of which enlarge the molecule, presumably entangling it in or attaching it to the adherend.

Good strength and flexibility characteristics in the boundary film formed between the adherend members by the isocyanate-based adhesives are also considered to be favorable contributions to good adhesion.

4. Polarity. The reaction of di- and polyisocyanates with various polyester and polyether glycols, their co-reactants in many adhesive applications, produces the relatively polar, highly hydrogen-bonded polyurethanes which wet, intimately contact, and show strong attraction for a variety of surfaces.

5. Step-off characteristics. Buist and Naunton<sup>13</sup> state that "polyisocyanate cements not only give a stronger (rubber-metal) bond but produce, possibly by a gradation of physical properties from the immovable rubber in contact with metal to the soft mass of the rubber, a condition in the rubber capable of withstanding greater fatigue."

6. Reaction with impervious surfaces. To explain the adhesion of isocyanate-based adhesives to impervious, apparently unreactive surfaces such as glass and metals, Bayer<sup>10</sup> suggested the reaction of isocyanate groups with the molecular film of tightly absorbed water always present on such surfaces, the reaction of the isocyanate groups with the oxyhydrate layer on metal surfaces, and isocyanate polymerization on (alkaline) glass. All of these processes

provide intimate contact if not actual chemical bonds between adhesive and adherend.

DeBell, Goggin, and Gloor<sup>12</sup> cite a striking example of the adhesion of isocyanates to glass: "One ingenious soul had patented a process for etching designs on glass by cementing on a metal stamping (carried on a mesh), and then tearing the mesh loose, whereby the surface of the glass pulled off."

## TYPES AND USE OF POLYURETHANE AND ISOCYANATE BASED ADHESIVE SYSTEMS

Polyurethanes and isocyanates are used in adhesives systems in several ways. The general use methods and systems, which include formulations containing both free or reacted isocyanate, are now reviewed.

### Method A (isocyanate primer)

A di- or polyisocyanate, usually in solution, is applied to the surface of an adherend prior to its contact with other adherend member(s) similarly coated.

Ex. 1. Buna-sulfur mixtures which are to be cemented are brushed with a solution of Desmodur R (III) and then vulcanized. In this way bond strengths of up to 1138 psi are realized.<sup>9,10</sup>

Ex. 2 MDI-50 (VII) affords heat-, fatigue-, impact-, oil-, and solvent-resistant bonds between metals and elastomers by press or hot air curing the green freshly milled or calendered stock against the metal which previously has been roughened (light sandblasting), solvent washed, thinly coated with MDI-50 and dried.<sup>16</sup> Humidity is an important factor in the degree of adhesion obtained. The following demonstrates the adhesion possible using this system with various elastomers and metals:

Adherend Members	Bond Strength (psi)
Neoprene W to steel	1100
Neoprene W to brass	1050
Neoprene W to stainless steel	1200
Neoprene W to aluminum	1325
Neoprene W to copper	950
Natural rubber (smoked sheet)	
to steel	1200
Butadiene-acrylonitrile rubber	
to steel	850

Ex. 3. Elastomer coatings may be adhered to synthetic fiber fabrics and other materials by Hylene M(VIII) or Hylene M-50 (IX) which are applied to the fabric as a 2% solution in toluene by dipping or spraying, drying, then applying the elastomer coating.<sup>17</sup>

Ex. 4. Degreased, sandblasted steel plates are coated by dipping in Leukonat adhesive (X). Green, filled stocks of Nairit, SKN-26 (butadiene-acrylonitrile), natural, and SKS-30 (butadiene-styrene) rubbers are freshened with solvent. Freshened rubber and coated metal are contacted and heated in a press.<sup>18</sup>

### Method B (conventional plastic or rubber vehicle + isocyanate)

A di- or polyisocyanate is mixed with a conventional elastomeric or plastic vehicle, usually in a dry, inert solvent. The combination is spread over the surfaces to be adhered which are then air-dried and contacted. Curing is at room or elevated temperatures.

DuPont<sup>16</sup> points out some special advantages in elastomer-to-metal adhesion which result from the use of an elastomeric vehicle with MDI-50 bonding cements. First, the elastomeric vehicle (usually the same as the adherend elastomer) covers the diisocyanate component in applied coatings, protecting it from moisture and providing longer but not unlimited\* useful life of cement-primed parts. Second, the elastomeric vehicle affords greater building tack and helps hold the adherend members in the desired assembly position.

Ex. 1. Natural rubber (pale crepe or smoked sheet), SBR, or neoprene Types GN, GR-M, or GR-MIO are broken down in Banbury mixers or on mills. Dry aromatic solvents such as xylene, toluene, or chlorobenzene (900 parts) are added and agitated to dissolve 100 parts of elastomer. Forty parts of MDI-50 (VII) are added to the elastomer solution with agitation. The cements are stored at room temperature: the rubber cement keeps 7 days, the SBR keeps 3 to 4 days, and the neoprene cement keeps 3 days.

\*MDI-50 elastomer cements slowly increase in viscosity with time, eventually gelling on prolonged storage at room temperature.<sup>16</sup>

The above cements applied at 10 to 15% of the fabric weight are excellent primers for the adhesion of elastomers to fabric. The cements can be applied to fabric by any of the conventional methods, and the primed fabric used after solvent removal or stored in a dry place until needed. The composite product may be cured by the methods conventionally used for curing rubber (press, oven, air pressure vulcanizers). High pressures are unnecessary and the good contact between the two surfaces is sufficient to produce a strong bond.<sup>21</sup>

Table 1 demonstrates the degree of adhesion obtained on the platen press curing of rubberized 10 oz cotton duck to square woven fabric samples made from rayon, cotton, and nylon. The duck had been skim-coated 90 mils with some typical tire carcass stocks made from neoprene GR-M, SBR, and natural rubber. The other fabrics were precoated with 20% by weight of the MDI-50 adhesive primers.<sup>21</sup>

Ex. 2. The adhesion of "Terylene," a polyester fiber, to rubber is greatly improved by

**Table 1. The Adhesion of Fibers to Elastomers via MDI-50 Priming Cement.<sup>21</sup>**

	Adhesive Primer					
	Neoprene		Natural		SBR/	
	GR-M/ MDI-50		Rubber/ MDI-50		MDI-50	
	A	B	A	B	A	B
Rayon to natural rubber	35	24	19	—	30	19
Rayon to neoprene GR-M	30	21	39	—	33	12
Rayon to SBR	37	26	28	—	35	17
Cotton to natural rubber	25*	16*	25*	16*	—	—
Cotton to neoprene GR-M	24*	16*	35*	21*	—	—
Cotton to SBR	29*	15*	27*	15*	—	—
Nylon to natural rubber	20*	11*	15*	8*	—	—
Nylon to neoprene GR-M	18*	9*	23*	12*	—	—
Nylon to SBR	22*	10*	20*	11*	—	—

A = adhesion at 28°C (lb pull/in. width)  
 B = adhesion at 95°C in water (lb pull/in. width)

Strip adhesion test (ASTM D413-39)

\* = Greater adhesion realized with more adhesive primer.

the addition of "Vulcabond" TX\* (XIII), a diisocyanate. Thus, a natural rubber stock containing all pigments (curing, reinforcing, processing agents) was made into a dough using Pool Rubber Solvent. Twenty-five percent by weight of "Vulcabond" TX was blended into this dough, and the mixture was spread onto "Terylene" fabric, topped with rubber stock on a calender, doubled, and finally platen pressured (200 psi) for 30 min at 141°C. Peel tests on 1-in. wide strips of this construction 24 hr later showed adhesions of 30.8 lb/in. (to initiate) and 22.0 lb/in. (average to maintain peeling). The control, minus "Vulcabond" TX, showed only 3.5 lb/in. adhesion in this test. Triphenylmethane-*p,p'*, *p''*-triisocyanate (III, X, XII) was similarly effective at the same concentration.<sup>22a</sup>

Ex. 3. Natural, "Hycar," "Paracril," and butyl and neoprene rubbers are bonded to seven metals/alloys with an adhesive comprising 50 parts of a chlorinated rubber ("Alloprene" B) and 100 parts of "Vulcabond" TX (XIII) dissolved in 150 parts of ethylene dichloride. Bonds to copper and "Monel" metal were inferior. Information is provided on the effect on bond strength of accelerator, loading types (carbon blacks, white fillers) in the bonded stocks, and the age of the fully formulated adhesive.<sup>22b</sup>

Ex. 4. A 3% rubber solution of a standard tire carcass compound was supplemented with 50% of "Vulcabond" TX (XIII) on the weight of rubber. Rayon cord dried for 1 hr at 100°C was then dipped into this cement, squeezed between glass rods, air-dried overnight, and baked 30 min at 100°C. This pretreated cord, carefully positioned in a metal jig to provide a concentration of 24 cords per in., was cured into a strip of rubber compound, which was then fatigued 4 days/80°C in a modified Roelig machine and finally tested for cord adhesion to the rubber. The following table shows how rayon cord primed with the "Vulcabond" TX-rubber cement outperformed a latex-resorcinol-formaldehyde priming cement, ("Vulcabond" T).<sup>13</sup>

The Relative Effectiveness of "Vulcabond" T and TX in Rayon Cord-to-Natural Rubber Adhesion.<sup>13</sup>

	Load (lb) to Pull out a Single Cord	
	Not Fatigued	After 4 days Fatigue at 80°C
"Vulcabond" TX cement	12.5	11.0
"Vulcabond" T cement	11.3	9.6

Ex. 5. For metal adhesion, polyisocyanates are best mixed into a solution of a synthetic or chlorinated rubber. The following table compares the adhesion of natural rubber tire tread to mild steel using a polyisocyanate priming cement ("Vulcabond" TX) with that obtained using a chlorinated rubber cement.<sup>13</sup>

"Vulcabond" TX Versus Chlorinated Rubber in Natural Rubber-Steel Adhesion.<sup>13</sup>

	Straight Pull (psi)	Impact Strength (ft lb)	Strength After Fatigue (%)
"Vulcabond" TX cement	835	220	90
Chlorinated rubber cement	785	116	20

Ex. 6. A priming cement for the high level adhesion (ca 28 lb/in.) of vinyl plastisol or film to nylon, "Dacron," rayon, or glass fabric is prepared from "Geon" 400 × 100\* (100 parts) or certain other polyvinyl chloride resins, dioctyl phthalate (60 parts), methyl ethyl ketone (380 parts) and DADI, dianisidine diisocyanate, (XIV) (10 parts). The adhesion is reported to be surprisingly independent of fabric construction and is obtained with a minimal effect on the fabric properties. The bond is reported to have been submitted to one million "S" flexes with no reduction in bond strength. The fabric is coated via normal solution-coating methods to about 0.8 oz/sq yd (dry weight) and is cured against PVC film or plastisol at 300 to 400°F for maximum adhesion (optimum adhesion 2 min/360°F).

\*Imperial Chemical Industries, Ltd., Manchester, England.

\*B. F. Goodrich Chemical Company, Cleveland, Ohio.

The primed fabric is stable for at least 60 days, and probably indefinitely; therefore, it need not be laminated to PVC film or coated with plastisol immediately.<sup>23</sup>

Ex. 7. The incorporation of PAPI, a polyisocyanate (XV), in specially compounded rubber-coating compositions has provided improved adhesion of rubber to nylon and polyester cord.<sup>24</sup>

### Method C (in situ polyurethane polymerization)

A di- or polyisocyanate is mixed with di- or polyhydroxy materials and the combination is (a) partially prereacted, or (b) allowed to react largely *in situ*, to form polyurethanes which contain free isocyanate groups capable of reacting with the adherend upon application. Dry solvents free of alcohols, carboxylic acids, etc. are used with these systems.

Ex. 1. Windemuth<sup>19</sup> teaches the practice of (a), a one part system. An isocyanate-terminated, viscous (in the melt), linear prepolymer is prepared from 2 moles of hexamethylene diisocyanate (II) and 1 mole of hydroxyl-terminated, linear polyester prepared from diethylene glycol and adipic acid. Two percent of hexahydrodimethyl aniline (a basic catalyst) is added to this prepolymer dissolved in dry benzene. The solution is applied to adherend members (e.g., the two ends of a leather drive belt) and dried. Subsequent brief exposure of the coated parts to moist air, followed by their contact under light pressure, results in a tough, flexible, rubbery bond in 2 to 3 hr.

Ex. 2. Liquid, isocyanate-terminated prepolymers prepared from diisocyanates such as TDI (I) and Poly B-D glycol (XXVII), a polybutadiene glycol, may be placed on an adherend directly or from solution and permitted to cure via the action of moisture in the air. Useful as rubber-fabric adhesive.<sup>79</sup>

Ex. 3. System (b), a two-part adhesive system, is exemplified in the following. One part of Polystal U-I [a 70% solution of Desmophen 900 (VI) in ethyl acetate] is mixed with 2–2.5 parts of Polystal UII [Desmodur HH (XI) in 75% ethyl acetate solution]. At room temper-

ature such a cement has a pot life of 1–2 days and with accelerator 3 hr. The setting time of this cement, containing accelerators, in wood adhesion is 4–5 hr at 10°C, 7 hours at 0°C, overnight at less than 0°C.<sup>10</sup>

Ex. 4. The M/M (Mondur/Multron) adhesive formulations are further examples of type (b) two component polyurethane adhesive systems. They are used for bonding metals such as steel, soft iron, aluminum, and magnesium to themselves and to each other. A recommended formulation for room temperature cures consists of 100 parts by weight of Multron R-12 (the polyester glycol resin component in 80% solids ethyl acetate solution) which is mixed with 120 parts of Mondur CB-75 (XXIX). Thus, Mondur CB-75 is a similar M/M counterpart of Desmodur HH in Polystal U-II. The full strength of steel bonds formed with this room temperature curing M/M system is 6800 psi and is achieved in 8 days. A recommended formulation for elevated temperature cures uses 200 parts of Mondur CB-75 per 100 parts of the Multron R-12 solution. Steel bond strengths of about 7800 psi are achieved in 3 hr at 195°F, 2 hr at 265°F, or 1 hr at 355°F. M/M adhesive gels 24 hr after mixing and cannot be reconstituted.<sup>20</sup>

Ex 5. "Tyrite" polyurethane structural adhesives are applied to adherends, then react or finish reacting *in situ* to form adhesive bonds. "Tyrite 7500" is two-part, 100% solids, pot life 6–10 min or 20–30 min depending on formulation, curing at room or elevated (e.g., 200–240°F) temperatures, for bonding rigid plastics, e.g., polycarbonate auto headlamps and RIM (reaction injection molded) urethane auto body panels.<sup>88a</sup> Three two-part moisture-curing systems have good storage life in the absence of moisture. In the presence of moisture, assembled objects are handleable in 4–6 hr, and have full cure in 1–10 days, depending on the particular system and the ambient relative humidity. "Tyrite 7411" is 100% solids, applied hot, for fabric and rigid plastics;<sup>88b</sup> "Tyrite 7602 is 64% solids, for general purpose use;<sup>88c</sup> and "Tyrite 7650" is 60% solids, with good initial grab, works well with polyethylene, polystyrene, and polyurethane foams as well as plastics, fabrics, rubber, prepared metals.<sup>88d</sup>

### Method D (polyurethane elastomer without or with added polyisocyanate)

Method D appears to be possibly the most important type of isocyanate-based adhesive system. It is similar to Method B in that a preformed, fully reacted, high molecular weight polymer is employed as a vehicle in the adhesive formulation. The strength of the vehicle holds adherend members in exact position after assembly until the full bond has formed. Method D differs from Method B in that its vehicle polymer is a polyurethane. A further difference is that the inherent adhesive character and strength of the polyurethane vehicle frequently enables its use without added di- or polyisocyanate. This strength may be realized in essentially amorphous compositions such as the thermoplastic polyurethane elastomers<sup>25</sup> or millable gums.<sup>26a,b</sup> Or it may be achieved with crystallizing urethane adhesive polymers.<sup>27,28</sup>

In the practice of Method D the high molecular weight polyurethane gum or thermoplastic resin is dissolved in a suitable dry, isocyanate-inert solvent. In the case of the polyurethane gums free di- or polyisocyanate is added to the solution. This is also sometimes done in the case of the thermoplastic polyurethane resins but frequently is unnecessary, in which case the use of dry isocyanate-inert solvents is also unnecessary.

Such cements are applied to adherend and allowed to dry to the desired degree of tackiness before contacting the adherend coated surfaces. Or, as in the case of the crystallizing thermoplastic polyurethane resins, the adhesive coating may be allowed to fully dry and crystallize. Subsequent heat activation of the coated adherend surfaces, then contact with each other, rapidly produces a strong bond.

So-called "anaerobic" polyurethane adhesives also appear to belong in the Method D category. This system combines urethane polyaddition chemistry with free radical-initiated addition polymerization to provide an interesting adhesive class. In practice, a polymerizable alcohol such as  $\beta$ -hydroxyethyl methacrylate is reacted with an equivalent amount of a diisocyanate such as TDI (I) or with an isocyanate terminated urethane prepolymer. An organic

hydroperoxide is then added to such intermediates and the formulation is packaged in oxygen-permeable containers (e.g., polyethylene) with the deliberate inclusion of air. The reason for this is that oxygen prevents the free radical-initiated polymerization of such unsaturated products. This preserves the adhesive on storage and after application on exposed substrate surfaces. But contact of the coated adherend surfaces buries the adhesive, excluding oxygen and allowing polymerization of the acrylate function with bond formation.<sup>68</sup>

Let's examine some representative examples of Method D adhesion. Examples 1—3 involve thermoplastic polyurethane elastomer vehicles. Examples 4—7 involve polyurethane gums.

Ex. 1. A solution of Estane 5703F2 (11.25 parts), Geon Resin 202 (3.75 parts), and tetrahydrofuran (85 parts) is prepared and brushed onto vinyl shoe sole and leather upper. After 1 min air drying the coated adherend surfaces are contacted under 20 psi pressure. Bond peel strength is 8.9 lb/in. after 15 min aging, and 29.0 lb/in. after 60 min aging. Good adhesion to other substrates including rubber, fabrics, and metal is claimed.<sup>27a</sup>

Ex. 2. Estane 5711, 5712, and 5713 resins are thermoplastic polyurethanes specifically designed for adhesive applications with a variety of substrates (e.g., wood, vinyl, leather, metal, rubber, fabrics, etc.) They are highly crystalline resins, soluble in practical solvents and characterized by high strength and toughness. At about 125, 140, and 160°F, respectively, these resins decrystallize to the amorphous state whereupon they become soft and rubbery with excellent wetting of a variety of substrates and a high degree of tack. At 75°F, the amorphous forms recrystallize in about 1/4, 2, and 24 hr, respectively, and become tackfree, very strong (3000, 5000, 9800 psi tensile, respectively), very extensible (790, 790, 730% ultimate elongation, respectively), and hard yet flexible. Suitable solvents for the various types include benzene, MEK, cyclohexanone, DMF, THF.

Estane 5712 applied from MEK cement between vinyl shoe sole and vinyl shoe upper stocks gave a peel bond strength of 40 lb/in.<sup>27b</sup>

Ex. 3. Desmocoll 176,<sup>28a</sup> 400,<sup>28b</sup> and 420<sup>28c</sup>



are primarily linear, thermoplastic polyurethane elastomer resins of "medium," "high," and "high" crystallization rates, respectively. They are supplied as small, light brown, talc-covered, pieces. The polymers have a density of 1.2–1.23 g/cc. This density and their stabilization by the hydrolysis stabilizer, Stabaxol 1, suggests that they are poly (ester-urethanes). They show outstanding adhesion to numerous materials including plastics, rubber, leather, fabrics, wood, metals, etc.

The following solvents dissolve some if not all of the foregoing Desmocoll adhesive polymers: methyl, ethyl, and butyl acetates, acetone, methyl ethyl ketone, methylene chloride, propylene dichloride, trichloroethylene, the monomethyl ether-acetates of ethylene glycol and 1,3-butylene glycol, etc. Toluene may be used as a dilution solvent.

Desmocoll 176 is compatible with such plasticizers as benzyl butyl phthalate (Unimoll BB), diphenyl cresylphosphate (Disflamoll DPK), and trichloroethyl phosphate (Disflamoll TCA). It has slight or no compatibility with dibutyl phthalate (Unimoll DB), dioctyl phthalate, triphenyl phosphate (Disflamoll TP), tricresyl phosphate (Disflamoll TKP), dibutyl adipate (Adimoll DB), benzyl octyl adipate (Adimoll BO), phenyl and cresyl alkyl sulfonates (Mesamoll, Dellatol MMA, Sintol T).

The foregoing Desmacoll polymers show compatibility with some or all of the following polymers to the extent that they give clear solutions and films: phthalic resins (Soft Resin MM, Alkydal BG), xylene-formaldehyde resin, cyclohexanone-formaldehyde resin (Synthetic Resin AFS), highly chlorinated terphenyl (Clophen Resin A60), terpene-phenolic resin (Durez 12603), acetyl cellulose (Cellit BL700), nitrocellulose, Desmocolls 12 and 22, nitrile rubber (Perbunan N), post chlorinated PVC (Rhenoflex), vinyl chloride-vinyl acetate copolymer (Vinnol), rosin esters (Pentalin A, Stabelite Ester 10), and coumarone resin.

In bonding strong substrates, and if solvent and greater heat-resistance are required in the adhesive bond, then the Desmocolls may be mixed with appropriate amounts of isocyanates such as Desmodur L (XVI), Desmodur R (III), and Desmodur RF (XVII).

Ex. 4. Royal M6482 and S-5210 adhesives can be applied to adherend surfaces from ketone solution and after drying may be heat or solvent activated. M6482 activates at 180–240°F and is a good adhesive for vinyl and for wood. S-5210 activates at 135–155°F and was designed for bonding man-made shoe upper stocks, leather, vinyl, etc.<sup>29</sup>

Ex. 5. One hundred parts of Daltoflex A-10 (XVIII) is mixed with 20 parts of Suprasec GA (XIX), 4.5 parts of Daltorol PRI (XX), and 25 parts of MEK solvent to provide a basic adhesive formulation. The Daltorol PRI increases open tack time while the Suprasec GA cross-links the system and improves its stability to steam, providing a vulcanizate of 2200 psi tensile strength, 200% elongation, and 1800 psi elastic modulus.

The Daltoflex A-10 system is recommended as an air-curing (2–7 day/25°C, <1 day/100°C) adhesive for textile applications (fabric-fabric, fabric-foam) since it affords good green strength and good hand, and for film-film lamination since it produces clear laminates which resist separation due to mechanical and thermal stress.<sup>30</sup>

Ex. 6 Multranil 176 polyurethane elastomer is dissolved at 20% by weight in a mixture of dry ethyl acetate and acetone, and 8.3 phr of Mondur TM (XII) (for natural and synthetic rubber adhesion) or 5 phr of Mondur CB-75 (XXIX) (for non rubber adhesion) is added. These combinations are versatile adhesives for bonding vulcanized rubber (natural and synthetic) to itself, leather, urethane, PVC, cork, wood, etc. Cure occurs at room temperature, and faster at elevated temperatures. At room temperature bond strengths (peel) are (immediate/after 3 days): rubber-to-rubber, 5.5–9.0/25; rubber-to-shoe sole leather, 5.5–7.3/24; shoe sole leather-to-shoe sole leather, 7.3–9.0/24; rubber-to-shoe sole leather, 9.5/24 lb/in. width.<sup>31</sup>

Ex. 7. "Bostik 7070" (100 parts) with "Boscodur No. 1" (5 parts) appears to be another example of a two part millable polyurethane gum adhesive system. It is recommended by the manufacturer as a laundering and dry cleaning resistant cement for bonding urethane sponge and urethane rubber. It is also recom-

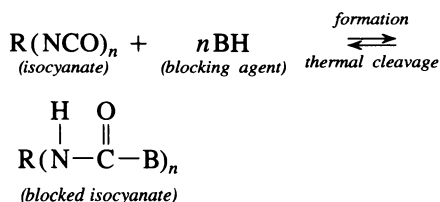
mended as an adhesive which provides strong elastic bonds with leather, natural and synthetic fabrics, cork, wood, Masonite, and a wide variety of porous materials.

The combination of Bostik 7070 and Boscodur No. 1 is reported to have a working life of about 18 hr. Although a hot bonding method (4 min at 130°F) is optional, the cement will cure at room temperature, developing maximum adhesion in 6 days.<sup>32</sup>

### Method E (blocked di- or polyisocyanate)

A stable, blocked di- or polyisocyanate in suspension, including aqueous suspension, or solution is applied alone (as in Method A), in combination with a conventional plastic or rubber vehicle (as in Method B), in combination with a di- or polyhydroxy material (as in Method C), or in combination with a pre-formed polyurethane vehicle (as in Method D) to adherend surfaces. The coating is dried, the coated adherend surfaces contacted, and the assembly heated to decompose the blocked isocyanate. This generates free di- or polyisocyanate which proceeds to bond the adherend directly and through reaction with the vehicle which may be a pre- or *in situ*-formed polyurethane. The cleaved blocking agent diffuses into the surrounding matrix or escapes into the air.

The formation and thermal cleavage of blocked isocyanates can be represented as follows:

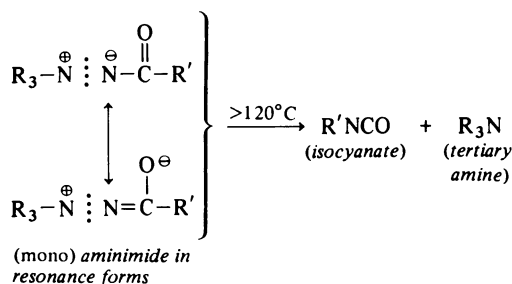


where  $n$  is usually 2, 3 and sometimes more. Cleavage temperatures range from ca 60 to 200°C depending on the compound.<sup>6b,33,62</sup>

“Blocked,” “masked,” or “pseudo” diisocyanates date back to German work of the 1940s.<sup>33</sup> The stability of blocked isocyanates toward active hydrogen substances enables their formulation and application in reactive media,

including water and alcohols. But usually the reactive medium must be removed by evaporation before the blocked isocyanate is heated to its decomposition temperature. Otherwise the generated isocyanate would be consumed by reaction with the medium before undergoing the intended reactions with adherend and reactive vehicle (if present). This may not be necessary if the isocyanate is more reactive with the adherend or vehicle than it is with the medium.

Commercially available blocked isocyanates have included: Hylene MP from duPont (XXI)<sup>34</sup> which is phenol-blocked MDI; Mondur S (XXII),<sup>35,36</sup> a phenol-blocked TDI adduct; Mondur SH (XXIII),<sup>36,37</sup> a cresol-blocked TDI trimer; and Experimental E-320 blocked isocyanate (XXIV),<sup>36,38,39</sup> a ketoxime-blocked tetraisocyanate, all from Mobay; and Isonate 123P (XXV)<sup>40</sup> which is  $\epsilon$ -caprolactam-blocked PAPI from the Upjohn Company. The Ashland Chemical Company has marketed a commercial chemical class called “aminimides” which act as isocyanate precursors, eliminating the problem of by-product phenol from the use of phenol-blocked isocyanates.<sup>65a,b</sup> Their chemistry relevant to this use, is as follows:



Aminimides are useful in a variety of adhesive systems for bonding tire cord and industrial fabrics, wire, and glass. They act as adhesive applicators in bonding rubber to tire cord. Considerable interest has developed in polyester cord dips, and the aminimide systems show great promise in bonding a variety of fabrics as well as wire such as stainless and carbon steel. Adhesion promoters for polyester fabric/rubber composites can be prepared from difunctional aminimides that react through polymerization with selective polyfunctional epoxides. Aminimides, functioning as isocyanate

precursors, offer many advantages over the usual phenol-blocked isocyanates, because these aminimides rearrange to isocyanates by simple thermolysis without yielding phenol as a by-product. This affords a safer industrial application of the tire cord adhesive.

Aminimides also offer processing advantages because of their water solubility. Aminimide pre-dips are easily prepared in water, so a variety of water-soluble surfactants, both anionic and cationic, can be used to enhance performance.

Polymers containing the pendant dipolar aminimide functional groups adhere strongly to glass. Low mole percents of aminimide monomers incorporated into polymethylmethacrylate significantly increase adhesion to glass. This property is valuable in polymers for bonding glass to glass or to other solid substrates.<sup>65a</sup>

The blocked isocyanate function of aminimides also allows their use as polyurethane adhesives. Thus, "bis (aminimides) crosslink with polyester or polyether diols to yield a range of elastomers, dependent upon the structure of the bis (aminimide) and the coreactant chosen. For example, bis (aminimides) mixed with polyhydroxyl components can provide stable, single package prepolymer compositions which yield polyurethanes on heating<sup>66</sup> without the problem of isocyanate moisture sensitivity which can plague polyurethane applications. Suggested applications include adhesives..."<sup>67</sup>

Ex. 1. Vulcanized neoprene and SBR can be adhered strongly to nylon and "Dacron" polyester fiber fabric by means of the following aqueous adhesive system:

"Hylene MP" dispersion (40%)	27.5 parts
Neoprene latex Type 635	173.0
Zinc oxide dispersion (50%)	15.0
Zalba emulsion (50%)*	6.0

\* A hindered phenolic antioxidant – duPont Elastomer Chemicals Dept.

This combination is spread or roller coated onto the fabric which is then allowed to dry. Bonds to sheet rubber stock can be made immediately after the treated fabric is dried or at

any time thereafter. When the sheet rubber is applied it should be held under moderate pressure of about 30 psi to provide intimate contact with the treated fabric and to prevent lifting if any gases are emitted during cure. Press cures of 20 to 40 min at 284°F are sufficient to cure the adhesive and most elastomer compositions being adhered. If a latex film is applied to the treated fabric, the assembly can be cured in a hot air oven at 250°F. Bonds strengths of 50 to 52 lb (nylon to neoprene, SBR), and 30 to 35 lb (Dacron to neoprene, SBR) are claimed. A chemical bond allegedly results between nylon and the diphenylmethane-p,p'-diisocyanate generated on the thermal cleavage of "Hylene MP."<sup>41</sup>

Ex. 2. A typical, excellent processing, aminimide rubber-to-fiber adhesive formulation recommended for pre-dipping polyester, nylon, and other polyamides comprises the following:<sup>65b</sup>

	Dip Bath Concentration 7.5% (parts by wt)
Aminimide	2.0
Epoxy Resin <sup>a</sup>	1.0
Surfactant <sup>b</sup>	0.112
Water	42.0

<sup>a</sup> XD-7160 (Dow Chemical Co.) or Epon 812 (Shell Chemical Co.).

<sup>b</sup> Aerosol OT (American Cyanamid Co.) or Aminimide 56203 (Ashland Chemical Co.).

The dip is prepared by dissolving the aminimide and surfactant in water with moderate stirring. The epoxy resin is then added with rapid stirring. The dip is ready for use and stable for 10–14 days. It is applied to the cord in a 1–3 sec dip. This is followed by drying in an oven at about 450°F (depending on cord type and desired properties) for about 45–60 sec. A second "cover dip" of conventional resorcinol-formaldehyde-latex emulsion is then applied followed by 45 sec drying at 450°F.

Following the foregoing procedure an Ashland Aminimide AL-X-300 (XXVIII) formulation yielded 3/8 in. H adhesion value for polyester cord (1300/39 × 9 twist) ranging from 46.3 lb (120 sec dwell at 405°F) to 58.7 lb (60 sec dwell at 465°F).<sup>65</sup>

### Method F (aqueous dispersion)

Most isocyanate- and polyurethane-based adhesive systems are now applied from solution in volatile organic solvents. But some day, perhaps not too far off, such systems may be impractical to use due to restrictions. Growing concern by ecologists for atmospheric pollution, and by safety agencies for worker welfare (explosion, fire, and toxicity) are factors to be increasingly reckoned with in all manufacturing processes which involve the use of large amounts of volatile organic solvent in open systems. One way around the problem would seem to be the use of aqueous polyurethane latex adhesives.

The preparation of polyurethane aqueous dispersions can be accomplished in several ways.<sup>83</sup> The procedure claimed to yield at present the highest quality products<sup>82a,b</sup> involves the reaction of an isocyanate-terminated prepolymer in a water-miscible solvent, e.g., acetone, with a diamine carboxylate or sulfonate. The resultant polyurethane ionomer solution is mixed with water which forms the dispersion and further chain-extends the polymer. Finally, the organic solvent is removed by distillation and can be recycled.<sup>84</sup> As in the case of the thermoplastic polyurethane elastomer adhesives, dispersions can also be prepared with different degrees of crystallinity in the polyurethanes depending on the nature of the prepolymer.<sup>82a,b</sup>

Alternatively, a linear, isocyanate-terminated, urethane prepolymer is prepared, sometimes with added solvent, from excess diisocyanate, macroglycol, dimethylolpropionic acid, and a tertiary amine. This product is dispersed in water and the prepolymer is then chain-extended with added diamine to produce an anionic aqueous latex comprising a high molecular weight poly(ester or ether-urethane-urea) with pendant, tertiary amine-neutralized carboxyl groups, dispersed in water.

Or thermoplastic polyurethanes made in solution or dissolved in solvents are emulsified in water, then solvent is removed. Or an isocyanate-terminated urethane prepolymer, possibly with hydrophilic branches, is blocked with an appropriate isocyanate-blocking agent, and emulsified in water together with a crosslinking agent.

Deterrents to the more widespread use of urethane latices appear to include their higher cost, as well as an inferior property level, relative to solution-applied polyurethanes, in those polymers that can be successfully made and used as aqueous dispersions. In addition, isocyanate-curing aqueous polyurethane dispersions for the most part require the use of the more expensive blocked isocyanates as well as substantial heat activation in place of the cheaper unmodified di- and polyisocyanates which cure effectively with little or no heating. Moreover, more energy and longer times are required to dry systems applied from water than those applied from volatile organic solvent. A change to water medium may require some unwelcome cycle modifications and line alterations. So, the motivation for polyurethane adhesive users to use aqueous latex forms has not been overwhelming, and unless a compelling situation develops or cheaper latices become available, the matter may remain that way. Whatever the outcome, several suppliers are now vigorously marketing aqueous urethane latex products. Let's examine some.

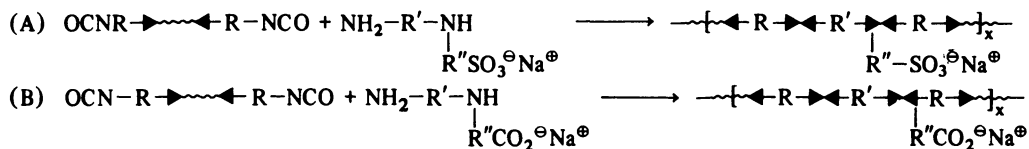
Ex. 1. BASF Wyandotte supplies a family of nonionic and ionic, stable, 50% solids, water dispersions of high molecular weight poly(ether-urethane) polymers.<sup>44</sup> These products reportedly contain some solvent in very low concentration, presumably toluene. They form continuous films when dried at room temperature, but film strength, abrasion resistance, and adhesion to substrates all improve when films or coatings are dried for several minutes at 250°F to 350°F.

The outstanding properties of coatings and adhesives based on these latices are claimed to be: wide range of flexibility or rigidity, flexibility retention to -40°F, excellent wear resistance, good adhesion to substrates, excellent film strength (540 to 4550 psi tensile strength) and elongation (300 to 750%), good color stability except in white and pastel shades, low toxicity, and low air pollution.

Ex. 2. Dainippon Ink and Chemicals, Inc., supplies Vondic 1010C, 1030, and 1310 high molecular weight poly(ether-urethane), 40% solids, aqueous dispersions.<sup>45</sup> Each product contains a small portion of toluene and the following features are claimed: 6 months stability

at room temperature; drying yields film of good physical properties (tensile strength after 16 hr at 25°C then 3 min at 100°C, 4900 psi, or 3 min at 140°C, 5300 psi; elongation, 480 to 530%; excellent abrasion resistance, flexibility, and tear strength; good retention of color and physical properties; fairly good solvent and water resistance).

Ex. 3 Verona (Bayer) supplies Impranil 4496 (DLN) color stable, 40% solids, thermoplastic, aliphatic poly (ester-urethane), anionic, aqueous dispersion.<sup>46,47</sup> Samples have appeared to contain a trace of solvent (acetone, MEK?). Presumably Impranil 4496 (DLN) contains a polyurethane ionomer and is prepared without added emulsifier, the polyurethane itself having its own emulsifier function. The incorporation of this function in the polyurethane chains as sodium (A) sulfonate or (B) carboxylate groups is seen in the following equations:<sup>47</sup>



This product is recommended for textile coating (skin, adhesive) via transfer coating. It is also claimed to be suitable for use as an adhesive in laminating woven materials to knitted goods or in laminating woven or knitted goods with polyurethane foam. Bondings are said to exhibit high elasticity, excellent cold flexibility, and good fastness properties. The supplier points out that the thermoplastic nature of Impranil 4496 allows it to be heat sealed and post-embossed.

Impranil 4496 particle size is 0.1–0.2 micrometers. Storage life is at least 6 months, but prolonged exposure above 140°F and cooling to less than 38°F must be avoided. Viscosity is 220 cps at 20°C (Brookfield, No. 1 spindle, 12 rpm). The latex yields continuous film with programmed drying (200°F, 230°F, 265–290°F) but adhesive applications accommodate 265–290°F directly.

Adhesion level may be increased by an additive, and Impranil 4496 is compatible with

selected acrylic dispersions and vinyl copolymers. It can be compounded with various colorants, pigments, and fillers.

Uncompounded 0.1 mm film shows 3550 psi tensile strength, 270 psi 100% modulus, and 700% ultimate elongation. Tensile strength drops to 565 psi after 400 hr of ultraviolet exposure (Xeno test) and to 2400 psi after hydrolysis exposure (14 days at 70°C (100% R.H.)).

Ex. 4. American Cyanamid supplies 10 Cyanabond textile adhesives<sup>48</sup> which are described as nontoxic, water-based, 30 or 40% solids, prereacted, polyurethane emulsions that provide highly durable bonds when applied to woven, knitted, or nonwoven fabrics. They have an acetic acid-type odor. They may be used on a wide variety of cellulosic and synthetic textile substrates. When applied by established processing techniques they form bonds of cloth-to-cloth and foam-to-fabric that

are highly resistant to the effects of dry cleaning and machine washing.

Types include Cyanabond Textile Adhesive U-270, U-271, U-251, U-253, U-273, U-274, U-255, and U-275 whose viscosities vary from water-thin liquids to mobile pastes of 90,000–95,000 cps viscosity (Brookfield LVF viscometer, No. 4 spindle, 6 rpm, 72°F). Storage stability is good for at least 6 months at 72°F.

In use Cyanabond Textile Adhesives, laminant fabrics, and foam must be completely dried and the laminated assembly then heated to 220°F for 5–10 sec for long term dry cleaning performance, or to 260°F for 15–30 sec for long term washability.

Stress-strain testing of Cyanabond Textile Adhesive U-270 at 30 in./min showed film to exhibit 1900 psi tensile strength, 655% ultimate elongation, and 730 psi 100% modulus.

Ex. 5. Refined Onyx Division, Millmaster Onyx Corporation supplies Karathanes 5A and 5HS, 50% solids, stable, aqueous, cationic

emulsions of fully reacted polyurethane.<sup>49</sup> The SHS product is reportedly a slight modification of the 5A product with much higher hydrolytic stability. Viscosity of Karathane 5A is typically 10,000 cps (Brookfield Model LVF, No. 4 spindle, 12 rpm). Karathane 5A films form on evaporating the emulsion water at ambient or elevated temperatures. They pass a flexibility test at  $-40^{\circ}\text{C}$ , and show 1500 psi tensile strength and 800% ultimate elongation. Karathane can be compounded (diluted, thickened, and pigmented). It must not be allowed to freeze.

Nopco Chemical, a Division of the Diamond Shamrock Corporation, also supplies polyurethane aqueous latices, as does the Witco Corporation.

### Method G (film and tape)

According to one article, tape and film adhesives are viewed as the "Cadillacs" of the adhesive industry in spite of their application in products of low overall cost.<sup>50</sup> By generally accepted definition, tape adhesives are those backed with a reinforcement or carrier while film adhesives are self supporting. Five reasons are advanced for their increasing acceptance, namely: very high reliability in use, very high degree of chemical and physical uniformity, ease of handling (which results in manufacturing cost reduction), significant waste reduction (since unused material can be stored for subsequent use), absence of mixing limitations (which allows realization of adhesive maximum physical properties).<sup>50</sup> To these can be added the same arguments advanced in favor of aqueous polyurethane latex adhesives over polyurethane cement adhesives in organic solvents—health, safety, and pollution abatement.

Various polyurethane types can be fabricated as elastomeric film and sheet.<sup>51</sup> The B.F. Goodrich Chemical Company supplies a family of thermoplastic polyurethane elastomers ("Estane") suitable for making such products,<sup>85</sup> and formerly marketed "Tuftane" film and sheet made from these polymers.<sup>52</sup> Currently, the Lord Corporation continues the manufacture and marketing of "Tuftane" film and sheet.<sup>86,87</sup> Stevens Molded Products has

also marketed such products in its "Hi-Tuff" line.<sup>53</sup> Thermoplastic polyurethane elastomer film and sheet are especially well suited for adhesive applications.

Ex. 1. "Tuftane" film is ideally suited for bonding emblems, numerals, and letters to many fabrics by heat and pressure alone. It also flame-bonds well to both polyester- and polyether-urethane foams at commercial bonding speeds. Since it contains no volatiles it does not require cure times as do solvent- or water-based adhesive systems. All "Tuftane" films can be adhered thermally by hot bar, thermal impulse, ultrasonic, or dielectric methods over a wide range of temperatures. Adhesive lamination to many substrates is possible by the heated drum, curing oven, or multiple can methods. Fabric bonds made with "Tuftane" are strong and withstand laundering and dry cleaning.

"Tuftane" film is available in several grades: as aromatic poly(ester-urethanes)—TF310, 312, 330, 360, 800, 840; aromatic poly(ether-urethanes) TF410, 420; aliphatic poly(ester-urethanes) TF100; aliphatic poly(ether-urethanes) TF110; low melt polymers TF260, 270; and special polyesters TF700, 710. It can be made in 1–90 mil thickness and  $\frac{1}{4}$ –80 in. widths.<sup>86,87</sup>

Ex. 2. Hi-Tuff HT-2000 series polyurethane thin-gauge sheeting and film "outperforms all other plastic film and thin gauge rubber sheetings where product applications require superior toughness, abrasion resistance, tear strength, flex life, low temperature flexibility, oil and gasoline resistance, and longer aging properties. Hi-Tuff sheeting can be vacuum formed, dielectrically sealed, and solvent or heat-bonded to substrates."<sup>53</sup>

### Method H (powder)

Powdered forms of plastics and rubbers are of worldwide interest. They allow the economical, low energy mixing of polymers with additives such as colorants, plasticizers, stabilizers, curatives, etc. The gentleness of powder mixing preserves polymer integrity, properties, and thus subsequent performance characteristics.

The fluidity of powders is another asset. It

permits conveyance, distribution, and application without benefit of other media such as organic solvents or water which must finally be removed and disposed. It obviates the need for melting the polymer to convey and distribute it.

The elimination of organic solvents in the application of coatings, saturants, sealants, and adhesives and its importance in environmental pollution abatement and worker health and safety has already been discussed in connection with aqueous polyurethane latex and polyurethane film adhesives. The absence of troublesome and expensive solvents in their application must rank near the top in the list of advantages associated with the use of powdered polymers, including adhesives.

Of the available polyurethane types, the "virtually crosslinked" thermoplastic polyurethane elastomers would seem to be best and ideally suited for supply and use in powdered form. Their uses include adhesive applications which exploit the advantages of the powder form.

Farbenfabriken Bayer (Ultramoll) and Dainippon Ink and Chemical Company (Pandel) supply powdered polyurethane. And duPont has explored these materials.

Ex. 1. Ultramoll PU is a highly flexible polyurethane based polymeric plasticizer in the form of a colorless and odorless powder of < 1000 micrometer particle size. It contains  $5 \pm 3\%$  of PVC and was especially designed for combination with PVC. It has  $72 \pm 3$  degrees Shore A hardness. Ultramoll PU yields improved adhesion strength in comparison with plasticized PVC in its injection molding as sole stock against shoe upper material.<sup>55</sup>

## POLYURETHANE STABILIZATION

Although polyurethanes are very extensively and successfully used polymeric materials with an excellent overall record of serviceability, sometimes they are misapplied or improperly formulated and their performance is disappointing. They are not high temperature polymers;<sup>56,57</sup> continuous service applications at more than about 120°C are not recommended. They are subject to hydrolysis;<sup>58,61,63,64,70-75</sup> other materials should be included for consid-

eration in applications which involve long term continuous immersion in water. They undergo autoxidation on thermal or ultraviolet activation.<sup>59,60</sup> Poly (ester-urethanes) are subject to microbiological degradation.<sup>61,76,77</sup>

The urethane linkage has a very practical degree of thermal stability but nevertheless it is not outstanding in this regard. Thermal dissociation at high temperatures is an inherent characteristic of the urethane linkage. It can be minimized by the exclusion of catalyst residues from the polymer. And to a degree by proper tailoring of the polyurethane structure.<sup>56</sup>

The addition of carbodiimides, e.g., Stabaxol 1, and particularly Stabaxol P (formerly Antioxidant PCD, Stabaxol PCD) which are supplied by Farbenfabriken Bayer, to poly (ester-urethanes) is one of the most effective ways to stabilize them against hydrolysis.<sup>58,71,72</sup> Also, polyurethane structure can be tailored for better hydrolysis resistance.<sup>58</sup>

Satrastab, developed by SATRA (Shoe and Allied Trades Research Association, Kettering England), is also claimed to be an effective hydrolysis stabilizer for formulated polyurethanes in poromeric footwear materials.<sup>63,64</sup>

The response of polyurethanes to thermally activated autoxidation depends on polymer structure. In general, polyurethane degradation by this mechanism is suppressed by the addition of antioxidant to the polymer. But in one study with a poly (ether-urethane) this was not true.<sup>57</sup> Ultraviolet initiated autoxidation is suppressed by a suitable screen (e.g., carbon black, titanium dioxide) or a combination of antioxidant and ultraviolet absorber.<sup>59</sup> Irganox 1010 and Tinuvin P (Ciba-Geigy) are particularly suitable antioxidant and ultraviolet absorbers, respectively, for polyurethanes. The polymer chemist can tailor polyurethane structures with enhanced resistance to ultraviolet-initiated autoxidation.<sup>60</sup>

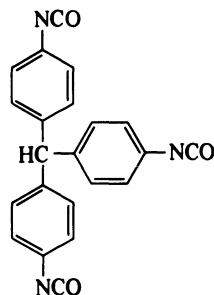
Inclusion of an effective fungicide in poly (ester-urethanes) prevents their degradation by microbiological action. Effective agents of this type include copper-8-quinolinolate ("Cunilate," Scientific Chemicals, "Quindex"-Nuodex Division, Heyden Newport) and N-(trichloromethylthio) phthalimide ("Fungitrol 11"—Nuodex).<sup>69</sup> Poly (ether-urethanes) resist microbiological degradation.

## HANDLING ISOCYANATE BASED ADHESIVES

Isocyanates unquestionably are highly reactive chemicals, which to a considerable degree explains their effectiveness in adhesive applications. Consequently, adhesive formulations containing isocyanates must have reasonable protection from contact with agents that combine with the isocyanate group, thus neutralizing it before it is able to react via polymerization or with the adherend. This dictates the use of essentially dry solvents which are nonreactive and free of reactive impurities, as well as avoiding exposure of isocyanate-containing adhesives to moisture during storage and excessive moisture during use.

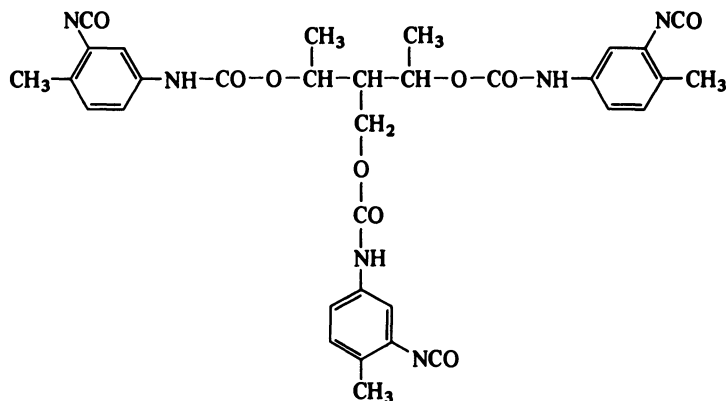
Reasonable caution in the use of materials containing free isocyanate including adequate ventilation in use areas and the prompt cleansing of body areas contacted is recommended by all isocyanate suppliers.

(III) Desmodur R — triphenylmethane-*p,p',p''*-triisocyanate — a 20% solution in methylene chloride.<sup>2,28e</sup>



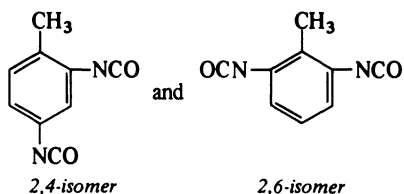
(IV) Desmophen 1200—a polyester prepared from adipic acid (3.00 moles), trimethylol propane or glycerine (1.00 mole) and 1,3-butylene glycol (3.00 moles).<sup>10</sup>

(V) Desmodur TH—adduct from 2,4-toluene diisocyanate (3.00 moles) and 3-methylol pentylene glycol-2,4 (1.00 mole);<sup>10</sup>



## IDENTIFICATION OF ADHESIVE COMPONENTS

(I) Toluene diisocyanate

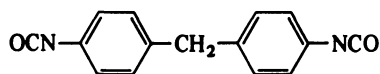


(II) Hexamethylene diisocyanate  
 $\text{OCN}-(\text{CH}_2)_6-\text{NCO}$

(VI) Desmophen 900—a polyester prepared from adipic acid (3.00 moles), trimethylol propane (4.2 moles).<sup>9,12</sup>

(VII) MDI-50—diphenylmethane-*p,p'*-diisocyanate—50 parts, orthodichlorobenzene—50 parts.<sup>16</sup>

(VIII) Hylene M—diphenylmethane-*p,p'* diisocyanate.<sup>17</sup>

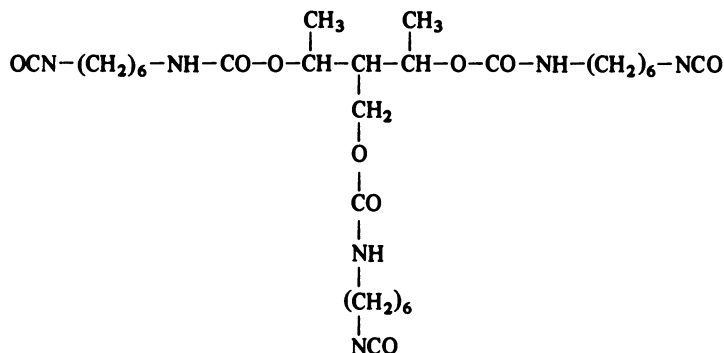


(IX) Hylene M-50—Hylene M—50 parts, orthodichlorobenzene—50 parts.<sup>17</sup>



(X) Leukonat adhesive—triphenylmethane-*p,p',p''*-triisocyanate—a 20% solution in dichloroethane.<sup>18</sup>

(XI) Desmodur HH—adduct from 1,6-hexamethylene diisocyanate (3.00 moles) and 3-methylol pentylene glycol-2,4 (1.00 mole):<sup>10</sup>

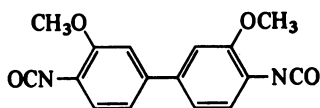


(XII) Mondur TM—triphenylmethane-*p,p',p''*-triisocyanate—a 20% solution in methylene chloride.<sup>42</sup>

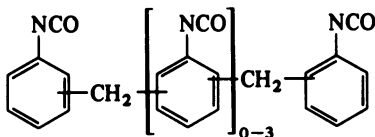
A 50% solution of diphenylmethane-*p,p'*-diisocyanate in xylene or orthodichloro-benzene.<sup>43</sup>

(XIII) Vulcabond TX—a polyisocyanate, principally a diisocyanate.<sup>22c</sup>

(XIV) DADI—dianisidine diisocyanate.<sup>24</sup>

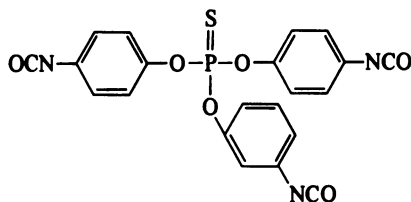


(XV) PAPI—polymethylene polyphenylisocyanate.<sup>24</sup>



(XVI) Desmodur L—equivalent to Mondur CB-75 (XXIX).<sup>28d</sup>

(XVII) Desmodur RF—a 20% solution of thiophosphoric acid tris (*p*-isocyanatophenyl ester) in methylene chloride.<sup>28f</sup>

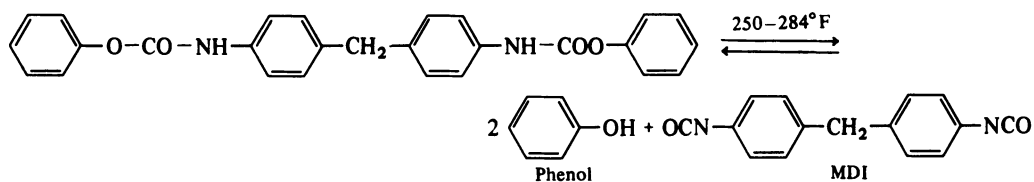


(XVIII) Daltoflex A-10—a viscous 45% solution in methyl ethyl ketone of a stable polyurethane elastomer containing no unreacted isocyanate.<sup>30</sup>

(XIX) Suprasec GA—A 75% solution in ethyl acetate of a resinous organic polyisocyanate containing a small amount of volatile free isocyanate.<sup>30</sup>

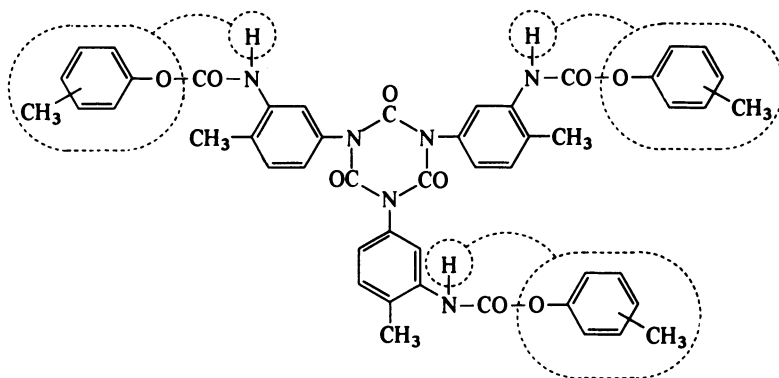
(XX) Daltrol PRI—a reactive liquid polyester.<sup>30</sup>

(XXI) Hylene MP—Methylene-bis-phenyl-(4-phenyl carbamate).<sup>34</sup>

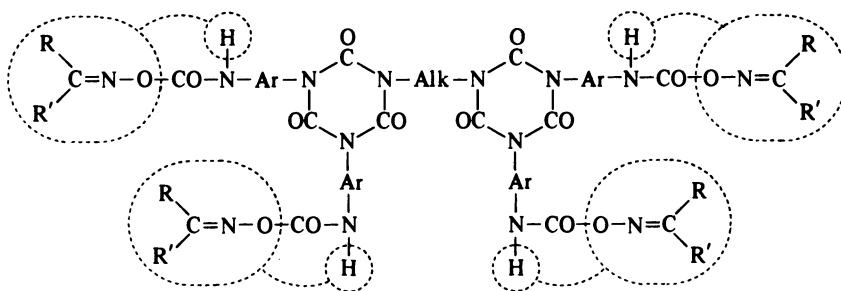


(XXII) Mondur S—a phenol-blocked TDI adduct.<sup>35,36</sup>

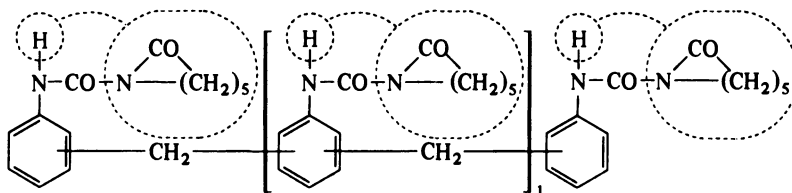
(XXIII) Mondur SH—a cresol-blocked TDI trimer,<sup>36,37</sup> presumably



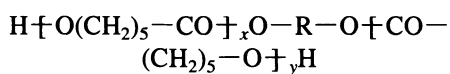
(XXIV) Experimental E-320 Blocked Isocyanate—a ketoxime-blocked tetraisocyanate.<sup>36,38,39</sup>



(XXV) Isonate 123P—ε-caprolactam—blocked PAPI.<sup>40</sup>



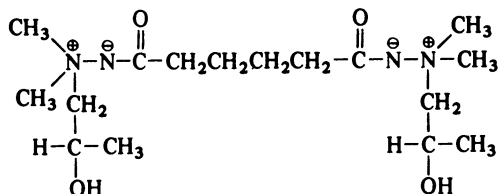
(XXVI) Poly (caprolactone) glycol.<sup>54</sup>



(XXVII) Polybutadiene Glycol (Poly BD Glycol).<sup>79</sup>

Poly BD R-15M and R-45M are hydroxyl-terminated polymers comprised solely of butadiene. Poly BD CS-15 and CN-15 are hydroxyl-terminated polymers with backbone structures comprised of butadiene-styrene and butadiene-acrylonitrile, respectively.

(XXVIII) Aminimide AL-X-300.<sup>65b</sup>



(XXIX) Mondur CB-75<sup>36</sup>—a TDI-trimethylol propane adduct, 75% nonvolatiles in ethyl acetate solution.

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# Polyvinyl Acetate Emulsions for Adhesives

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Polyvinyl acetate has been available commercially in the United States since the 1930s. Growth was slow until the 1940s, when polyvinyl acetate emulsions were introduced. The volume of resin consumed has since grown from a negligible amount in 1945 to 1.7 billion pounds currently.

The adhesive industry is one of the most important outlets for polyvinyl acetate. An estimated 500 million pounds was used domestically in adhesives in 1987. Polyvinyl acetate also goes into surface coatings, caulks, etc.

Polyvinyl acetate came into widespread use in adhesives in the 1940s as a synthetic resin substitute for hide glue. Superior properties of the synthetic resins offset their higher price. Polyvinyl acetate adhesives were adaptable to new high-speed machinery in the paper converting and packaging fields and were enthusiastically received. They found a place in wood adhesives and later were introduced in the familiar household "white glue." Significant advances have taken place in polyvinyl acetate technology. A large number of sophis-

ticated polymer and copolymer products have been commercialized to meet the needs of changing technology.

The excellent adhesion of polyvinyl acetate emulsions to cellulosic and other materials gave rise to an abundance of applications, including bookbinding, paper bags, milk cartons, drinking straws, envelopes, gummed tapes, convolute tubes, folding boxes, multiwall shipping bags, labels, foils, film and paper board decals, cigarette tips, lagging compounds, wood assembly, padding, automobile upholstery, pencils, leather binding, and tile cements.

Because of their relatively low cost, ready availability, wide compatibility, and excellent adhesive characteristics, many polyvinyl acetate resins, solutions, and emulsions are treated as commodity items by the adhesives industry. Among the many U.S. manufacturers of polyvinyl acetate based resins are the following major producers: Air Products, H. B. Fuller, National Starch, Reichhold, Rohm and Haas, Union Carbide, Union Oil, and W. R. Grace. The resulting competition has benefited adhesives formulators with low prices, good qual-

ity, new improved products, and greater technical service from the resin manufacturers. Price variation is a common experience in this competitive market. Grade of resin and volume are important factors in selling price.

Emphasis on the use of polyvinyl acetate in the adhesives industry alone gives a rather confining picture of the resin. Its use in other industries actually depends on its adhesive, binding, and film properties as much as it does in the adhesives industry.<sup>1</sup> Among the major outlets for polyvinyl acetate emulsions are interior and exterior flat paints, particularly for masonry surfaces. Leveling and color retention are the outstanding properties of these coatings. The textile industry utilizes polyvinyl acetates, mostly in emulsion form, for finishes that impart durability, strength, and "hand" to woven cotton and other fabrics. Emulsions of vinyl acetate and comonomers serve as binders for nonwoven or bonded fabrics. The paper industry uses small particle size polyvinyl acetate emulsions as pigment binders for clays in paper and paper board coatings.

### Monomer

Vinyl acetate is the most available and widely used member of the vinyl ester family. This colorless, flammable liquid was first prepared in 1912. Liquid-phase processes were commercialized early in Germany and Canada,<sup>3</sup> but these have been replaced generally by vapor-phase processes. Earlier commercial processes were based on the catalyzed reaction of acetylene with acetic acid. The more recent technical development is the production of vinyl acetate monomer from ethylene and acetic acid. Palladium catalyst is used for the vapor phase process. The ethylene route is the dominant route worldwide.

Vinyl acetate is manufactured in the U.S. by Borden, Celanese, duPont, Union Carbide, and U.S.I. Chemicals. Its properties and reactions are reviewed in trade bulletins of the suppliers,<sup>6-9</sup> and more extensive discussions are presented in technical literature.<sup>10-14</sup>

Domestic capacity for production of vinyl acetate in the U.S. was estimated to be 2.4 billion pounds per year in 1987.

The discussion that follows covers (1)

aqueous dispersions and (2) solid resins derived from aqueous dispersions.

### Polymerization

Early studies of the polymerization of vinyl acetate and the structure and properties of the polymer were made during the first quarter of the century.<sup>15,16</sup> The first patents on polymerization were also issued during that period.<sup>17,18</sup> The real commercial development on the continent began in 1925. Commercial polymerization was underway by 1929.<sup>19-21</sup> Since then, a wealth of technical literature has been published dealing with polyvinyl acetate.<sup>22</sup> A particularly comprehensive article and bibliography on vinyl acetate polymerization and polymer properties is found in the "Encyclopedia of Polymer Science and Technology."<sup>12</sup>

Vinyl acetate polymerizes by a free-radical mechanism. Free radicals generated by the decomposition of organic peroxides such as benzoyl or hydrogen peroxide or of inorganic "per" salts such as potassium or ammonium persulfate are commonly used to initiate polymerization. Reactions ordinarily are accomplished at temperatures above room temperature. Other techniques of polymerization have been used to make novel products; low temperature redox polymerization, irradiation, and ionic catalysis.

High molecular weight and essentially linear polymers, controlled particle size in the case of emulsions, and even polymers with spatially regulated structures are available. Vinyl acetate copolymerizes with many other vinyl monomers. Acrylate esters; vinyl chloride and vinylidene chloride; dibutyl and other dialkyl maleates and fumarates; crotonic, acrylic, methacrylic and itaconic acids; vinyl pyrrolidone; and ethylene are commercially important comonomers.<sup>2</sup> A monomer that does not combine with vinyl acetate alone may be combined by use of a third monomer. "Grafting" can be used with monomers such as styrene that do not copolymerize with vinyl acetate.

Laboratory processes for the polymerization of vinyl acetate and some of the other vinyl esters are readily available from monomer suppliers and in the patent literature. Commercially, vinyl acetate polymers have been made

by all of the standard methods: bulk, suspension, emulsion, and solution.<sup>2,12</sup> Manufacturing processes are also available.<sup>12</sup>

## Emulsions

Polyvinyl acetate is most widely used in the form of a dispersion of solid resin in water. These dispersions are produced by emulsion polymerization and are more commonly termed *emulsions*. In 1987, production volume was on the order of 1.7 billion wet pounds for all uses and 500 million wet pounds for adhesives. Most products for adhesives are sold at 55% solids at a sufficiently high viscosity level to facilitate use. These products are manufactured by one of several techniques<sup>23-26</sup>—batch, continuous, or delay feed, depending on properties desired. The large volume usage depends not only on the outstanding adhesive properties of the resin but also on the excellent compatibility of the emulsions with many modifying agents.<sup>1</sup>

The properties, uses, and methods of formulating emulsions are graphically and comprehensively described in the trade literature, which is an excellent source of information. Most manufacturers specify properties of their emulsions in terms of percent solids, emulsion viscosity, pH, acid content, percent unreacted monomer, and density. Other properties generally described are particle size, molecular weight, film properties such as clarity, water and grease resistance, and tolerance of the emulsions to various organic and inorganic chemicals.

Although all components of an adhesive (film formers, plasticizers, viscosity modifiers, tackifiers, solvents, fillers, and surfactants) have strong influence on the performance of the adhesive, the film formers or polymer emulsions are the most important. This is because the polymers, through molecular weight and structure, contribute such vital properties as tensile strength, toughness, flexibility, specific adhesion, chemical resistance, mechanical stability, and compatibility with modifiers.

The fundamental properties of the polymer background determine the suitability of a given type of emulsion for a particular market. Though styrene butadiene and acrylics are widely used, the largest portion of the U.S. ad-

hesives market is served by vinyl acetate and its copolymers.

## ADVANTAGES OF POLYVINYL ACETATE EMULSIONS

### Adhesion to a Wide Variety of Surfaces

Polyvinyl acetate resins adhere well to more surfaces than most other adhesive bases. Polyvinyl acetate homopolymers bond particularly well to wood and paper substrates. Copolymers of polyvinyl acetates adhere to, or can be compounded to adhere to, a wide variety of plastic film and metal foils that are frequently laminated or combined with paper and wood.

### High Molecular Weight

Polyvinyl acetate emulsions have the advantage of combining high molecular weight with low usable viscosity. Since the molecular weight of the polyvinyl acetate does not affect the viscosity of the emulsion, it is possible to design adhesive bases which have high cohesive strength and toughness, and yet also have viscosities that allow application by roller, spray, or extruder.

### High Solids

The emulsion form of polyvinyl acetate also allows the production of high solids (55%) adhesives at low viscosities. It is possible, therefore, to make rapid-setting, low shrinkage adhesives at viscosities which permit them to be easily applied by roller, spray, or extruder. Recent emulsions contain 65–66% solids while maintaining low viscosity.<sup>27</sup>

### Rapid Setting Speeds

In the case of emulsion-based adhesives, the loss of a relatively small amount of water will cause the inversion of the emulsion and rapid setting of the adhesive. This contrasts favorably to solution-based adhesives, both water and organic solvent types, which require that most of their solvent be lost to the atmosphere and/or absorbed into the substrate before they become tacky enough to hold the substrate together. In fact, even more solvent must be lost



before strong, fiber-tearing bonds can be obtained.

### **Easy Modification of Water and Solvent Resistance**

Polyvinyl acetate can be protected with colloid systems, surfactant systems, or a combination of both.<sup>12</sup> By varying the protection system, it is possible to produce adhesive bases whose relative water resistance will differ in range from water remoistenable to water resistant (24 hr) and even to boiling water resistant. The choice of a protection system used in an adhesive base will also affect the degree of solvent resistance.<sup>40</sup>

### **Good Machining Characteristics**

Polyvinyl acetate-based adhesives have a high degree of mechanical stability and machine well in many different modes of application. At the same time, they will set very rapidly.

### **Ease of Compounding**

Polyvinyl acetate emulsion adhesives can be compounded using very basic mixing equipment and procedures. Many resins, plasticizers, solvents, and fillers can be blended directly into the emulsion without preemulsifying or predispersing the additives. The ability to modify polyvinyl acetate with a wide variety of additives makes the adhesives more versatile and allows adhesion to a wider number of substrates than adhesives made from other resin bases.

### **Resistance to Microorganisms**

Dried polyvinyl acetate adhesive films are highly resistant to attack by microorganisms. The addition of biocides will prevent attack of microorganisms on a liquid emulsion or on a dried adhesive film when animal or vegetable modifying ingredients have been added to the emulsion.

### **Resistance to Oxidation and Ultraviolet Radiation**

Polyvinyl acetate is a saturated molecule and is therefore not subject to degradation by oxygen, ozone, or ultraviolet radiation.

### **Low Toxicity**

Polyvinyl acetate adhesives have a low degree of toxicity and have been used in food packaging for decades. They have been approved for this use by the Food and Drug Administration.

### **Minimal Environmental Impact**

Polyvinyl acetate emulsions, as a class, have a low biological and chemical oxygen demand.

## **HOMOPOLYMERS AND COPOLYMERS**

### **Homopolymers**

The early polyvinyl acetate emulsions were homopolymers protected with partially hydrolyzed polyvinyl alcohol. These high molecular weight polymers had great strength and set rapidly to hard, horny films. Today, these homopolymers are the workhorses of the industry due to their excellent adhesion to uncoated paper, wood, concrete, ceramics, and glass. In addition, they exhibit a fair degree of water sensitivity. This allows them to be easily cleaned from equipment and permits their use in remoistenable adhesives.

### **Copolymers**

Since polyvinyl acetate is a stiff material, the need for more flexible versions became apparent early in the development of the industry. The adhering of plastic films to paper and the bonding of resin-coated paperboard in packaging applications are two examples of this need for greater flexibility.

Flexibility can be obtained either by compounding with an external plasticizer or by copolymerizing with a suitable monomer. When a homopolymer adhesive is flexibilized with external plasticizers and/or solvents, the resultant bonds frequently fail on aging because of plasticizer migration. This may occur in any of three ways: (a) the plasticizer may migrate into the plastic substrate, leaving a brittle adhesive which loses its bond in as little as 7–10 days; (b) if the substrate is plasticized PVC, the plasticizer in the substrate may migrate into the adhesive, softening it to the point where it has little cohesive strength; or (c) the plasticizer in the substrate may migrate to the inter-

face and, in effect, act as a release agent due to incompatibility with the polyvinyl acetate.

When a polyvinyl acetate emulsion is flexibilized internally with a comonomer, the plasticization is permanent and nonmigratory. This is because the comonomers are part of the main polymer chain, often with bulky side groups, increasing the freedom of rotation of the chain. The resulting softening and polymer mobility allows better adhesion to plastic surfaces.

Monomers which are copolymerized with vinyl acetate include alkylacrylates, alkylmaleates, fumarates, and ethylene. The level of comonomers may vary from a few weight percent of the copolymer to as much as 70 weight percent.

### Ethylene vs. Ester Comonomers

The early copolymers of vinyl acetate with dibutyl maleate or acrylate esters offered distinct advantages over the homopolymer in their ability to adhere to a vast number of difficult-to-bond surfaces. However, they also had disadvantages, e.g., poor heat resistance, relatively low strength, rather slow setting speed, and comparatively poor machinability. The introduction of vinyl acetate-ethylene copolymers changed this picture considerably. This class of emulsion had all the benefits of homopolymers in strength, machinability and heat resistance in addition to better adhesion characteristics than those of the ester copolymers.

Ethylene is a much more effective internal plasticizer for polyvinyl acetate than are dibutyl maleate and acrylate comonomers. Compared with dibutyl maleate, smaller amounts of ethylene are necessary to decrease the glass transition temperature of the homopolymer (Fig. 1). Vinyl acetate-ethylene copolymers also have much higher tensile strength than vinyl acetate-dibutyl maleate copolymers at equivalent glass transition temperatures (Fig. 2). In fact, the ethylene copolymer emulsion has a higher tensile strength than vinyl acetate-dibutyl maleate even though its glass transition temperature is lower and its percent elongation is about the same (Table 1). In addition, the vinyl acetate-ethylene copolymer has the same heat or creep resistance as the homopolymer and much better creep resistance than the vinyl acetate-dibutyl maleate type (Table 2). It should

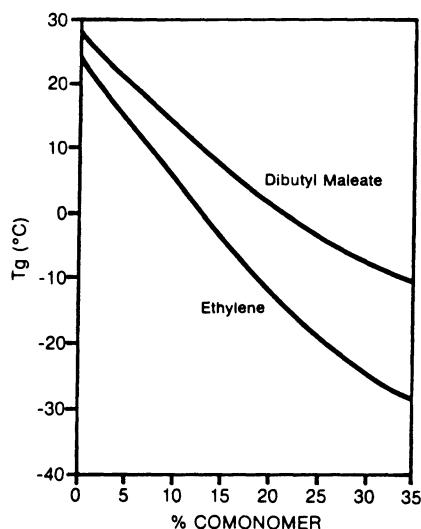


Fig. 1. Comonomer levels required to plasticize polyvinyl acetate.

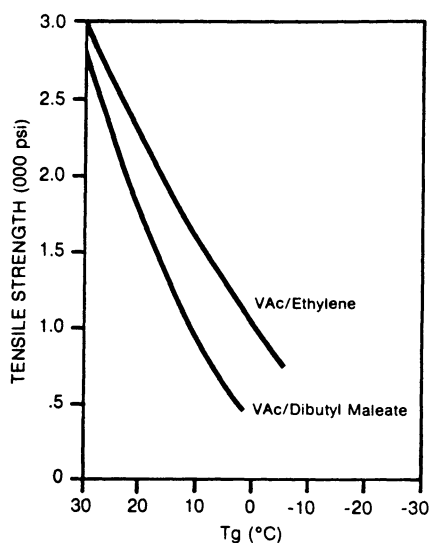


Fig. 2. Effect of  $T_g$  on vinyl acetate copolymer film tensile strength.

Table 1. How Comonomers Affect Copolymer Film Properties.

Property	VAc/Ethylene	VAc/Dibutyl Maleate
Tensile Strength (psi)	960	618
$T_g$ (°C)	0	6
Elongation (%)	1660	1550

**Table 2. Relative Creep Resistance of Polyvinyl Acetate Emulsions.**

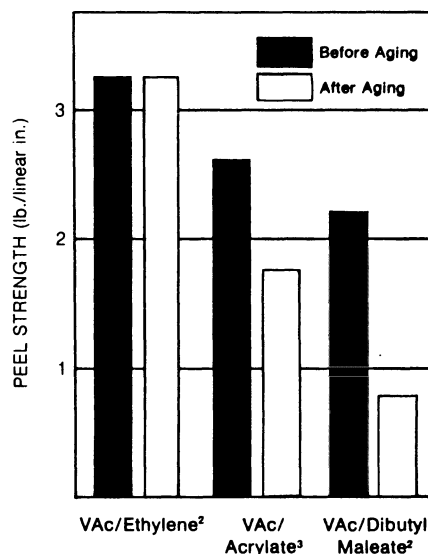
Emulsion Type	Creep (mm/min)
Homopolymer	0.02
VAc/ethylene	0.02
VAc/dibutyl maleate	7.6
Homopolymer and 10% DBP <sup>a</sup>	0.6
VAc/ethylene and 10% DBP <sup>a</sup>	0.6

<sup>a</sup>DBP = Dibutyl phthalate.

be noted that when it is plasticized with 10% dibutyl phthalate, it still has less creep than the neat vinyl acetate-dibutyl maleate and is equal to a homopolymer containing an equal amount of plasticizer.

VAE (vinyl acetate-ethylene) emulsions do not require as much plasticizer to obtain a strong bond to PVC as do vinyl acetate-dibutyl maleate and vinyl acetate-acrylate (Fig. 3). Importantly, these copolymers do not soften nearly as much as the other copolymers when plasticizer is added. This means that as laminations of films to cellulosic substrates age, the bond made by the VAE will not lose its cohesive strength and weaken (Fig. 4).

Certain properties may best be explained by examining the molecular structure of polyvinyl acetate and some of its copolymers. Fig. 5 compares polyethylene and polyvinyl acetate homopolymers. Polyethylene is, of course, a flexible polymer, whereas polyvinyl acetate homopolymer is hard and brittle because steric hindrance between alternate acetate groups restricts movement of the molecules. A copolymer of vinyl acetate containing 25 weight

*Effect of Accelerated Aging<sup>1</sup> on Polyvinyl Acetate Copolymers*

1. Bonds aged one week at 120°F.

2. Protective colloid: polyvinyl alcohol.

3. Protective colloid: cellulosic.

Fig. 4. Peel strength of PVC to cloth bonds.

percent of dibutyl maleate may be visualized as a polyethylene chain with acetate groups on every other carbon atom for 16 atoms on the chain, and a butyl ester group on the 17th and 18th carbon atoms (Fig. 6). These resins are flexible because the bulky pendant butyl ester groups allow intermolecular movement and also separate the chains of polymers so that they can slip past one another rather easily. This accounts for the higher degree of creep in a vinyl

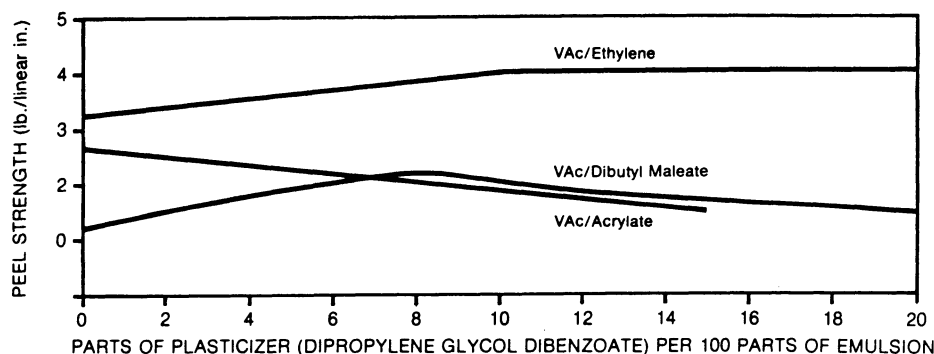
*Effect of Plasticizer on Polyvinyl Acetate Copolymers*

Fig. 3. Peel strength of PVC to cloth bonds.

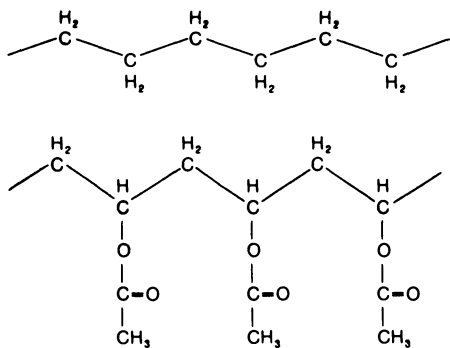


Fig. 5. Polyethylene and polyvinyl acetate homopolymers.

acetate-alkylmaleate or vinyl acetate-alkylacrylate copolymer. In the case of vinyl acetate-ethylene copolymers, the flexibility is achieved through much less steric hindrance, because the acetate groups are not attached to alternate carbons, and movement is not restricted along the molecule (Fig. 7). Since the large, bulky side chains are not present to achieve flexibility, these polymers exhibit higher cohesive strength and much less creep. The use of polymer  $T_g$  as a guide to latex specification for adhesive purposes has been described.<sup>39</sup>

Another feature of the vinyl acetate-ethylene

copolymers is that they have greater resistance to alkalis and acids than the older copolymers. When acetate groups are present on alternate carbons, the hydrolysis of one acetate group by alkali exposes the next acetate group. The reaction proceeds rapidly down the entire chain, unzipping the polymer. With vinyl acetate-ethylene, the zipping is interrupted; therefore, rapid hydrolysis does not take place. In fact, test films of vinyl acetate-ethylene have been exposed to weak alkalis and acids for more than a year without showing signs of deterioration.

### Other Factors Affecting Adhesive Properties

Polyvinyl acetate emulsions are among the most versatile bases for adhesives because they can be modified during polymerization in many more ways than other resins used for adhesive compounding. Major changes can be made to the adhesive properties of polyvinyl acetate by changing the method of protecting the emulsion, by varying the glass transition temperature ( $T_g$ ), by modifying the degree of branching, or by adding a variety of functional groups. These modifications may be made singly or in any combination of the above four.

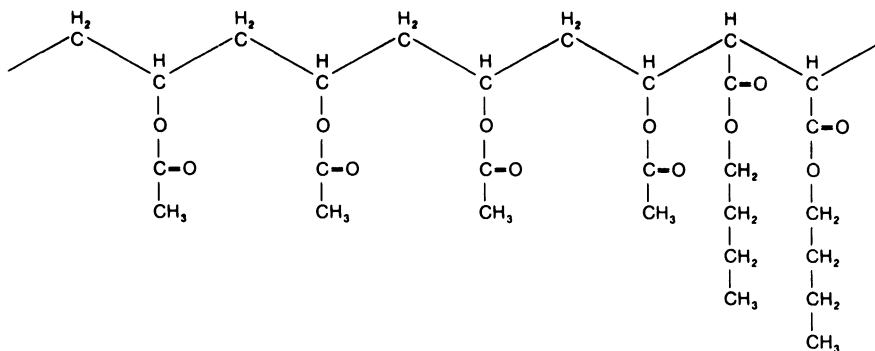


Fig. 6. Vinyl acetate-dibutyl maleate copolymer.

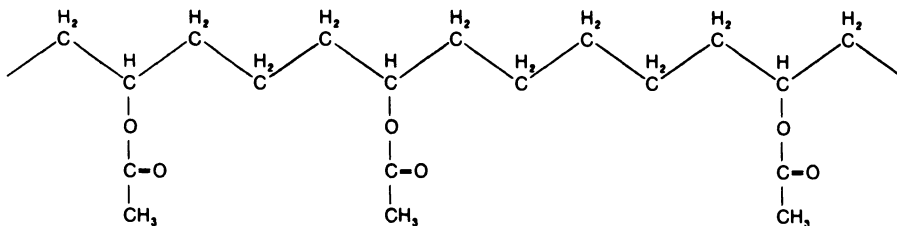


Fig. 7. Vinyl acetate-ethylene copolymer.

As an indicator of the technical significance to the adhesive industry of these emulsions, one finds 2,333 patents describing them and their uses listed in chemical abstracts from 1972 to the present. A total of 28 review articles have appeared worldwide in that time.<sup>28</sup>

### Protection by Colloids and/or Surfactants

Polyvinyl acetate can be protected with colloid systems, surfactant systems, or a combination of both. The type and amount of protection used in the polymerization of polyvinyl acetate have a great bearing on the physical properties of the resin and on the working characteristics of the dispersion.

Table 3 compares emulsion and dried film properties controlled by the protection system. Since partially hydrolyzed polyvinyl alcohol is a poor emulsifier compared with a surfactant, a polyvinyl acetate emulsion protected with this colloid would have a combination of large particles and a rather wide particle size distribution. This combination of particle size and distribution yields an emulsion that does not change its viscosity very much as it experiences high shear conditions. On the other hand, an emulsion which is protected solely with a surfactant (nonionic surfactants are generally

used with polyvinyl acetate) has a fine particle size and a rather narrow particle size distribution.

Polyvinyl alcohol is a water-soluble molecule. It will therefore contribute a high degree of wet tack to an emulsion that is not possible with surfactant protection. Polyvinyl acetate emulsions protected with partially hydrolyzed polyvinyl alcohol have a combination of properties usually described as "good machining," which include good flow, clean running, easy cleanup, and nonslinging or nonspitting. These properties are generally not present in emulsions protected solely with surfactants. Surfactant-protected emulsions are much more thixotropic than polyvinyl alcohol-protected emulsions, and become thin under high-shear conditions.

Polyvinyl acetate emulsions set by losing water through evaporation into the air and also by absorption into the porous substrates to which they are applied.<sup>38</sup> The polyvinyl acetate spheres in the emulsion pack together and form capillaries which aid in the transport of the water out of the film. The fine particles in an all-surfactant system form small capillaries which drive water out at a rather rapid rate. In a polyvinyl alcohol-protected system, the variously sized particles pack tighter and form much finer capillaries, which drive the water out at a much more rapid rate. This causes the emulsion to form a film and set more rapidly than an all-surfactant system.

The particles of polyvinyl acetate coated with partially hydrolyzed polyvinyl alcohol cannot form a very tightly coalesced film. This is because polyvinyl alcohol has a higher  $T_g$  than, and is not compatible with, polyvinyl acetate. As a result, the dried film will have a hazy, flat appearance. This contrasts with a surfactant-protected acetate, which will coalesce more tightly and will therefore form a clear, glossy film. The dried film of a surfactant-protected emulsion will be much less water sensitive than that of a polyvinyl alcohol-protected emulsion. This is attributable to the water solubility of polyvinyl alcohol, and can be overcome to various degrees by crosslinking of the PVOH after film formation has occurred.<sup>33,36,37</sup>

Emulsions which combine surfactant and colloid protection will display properties that

**Table 3. How the Protection System Affects the Properties of an Adhesive Base.**

<i>Emulsion Properties— Colloid Protected</i>	<i>Emulsion Properties— Surfactant Protected</i>
Large particle size	Fine particle size
Wide particle size distribution	Narrow particle size distribution
Strong wet tack	Poor wet tack
Good flow	Poor flow
Good machining	Relatively poor machining
Rapid setting	Relatively slow setting
Near-Newtonian rheology (does not shear thin)	Thixotropic rheology (thins with shear)
<i>Film Properties— Colloid Protected</i>	<i>Film Properties— Surfactant Protected</i>
Hazy film	Clear film
Flat film	Glossy film
Water sensitive	Water resistant

fall somewhere between those exhibited by colloid systems or surfactant systems alone.

The effect of the protection system is illustrated in Table 4, which shows the properties of three VAE copolymers with the same level of ethylene and the same  $T_g$ . One is PVOH protected, one is surfactant protected, and the last is protected by a combination of surfactant and cellulosic.

The first major difference among the three is that the PVOH-protected emulsion is incompatible with borax and highly soluble dextrin, whereas the other two emulsions can accept these compounds without breaking. In addition, the PVOH-protected emulsion exhibits less water resistance and more water spotting. Water resistance denotes the ability of a lamination between two substrates, such as kraft paper or cloth, to maintain its integrity or bond strength after immersion in water for a specified time. Water spotting describes the appearance of a dried film or emulsion after water is placed on that surface. A good or excellent film would not blush as rapidly as would the film indicated as fair. A lamination or bond made with the PVOH-protected emulsion has good water resistance, yet can be cleaned from machines more readily than the other two emulsions. The water resistance of the PVOH-protected emulsion permits its use in glue laps, bag-seam adhesives, and polyvinyl chloride-laminating adhesives.

The PVOH-protected emulsion has a greater wet tack because of the water soluble polyvinyl alcohol in its continuous phase. As discussed earlier, polyvinyl alcohol protection contributes to finer capillary formation and thereby promotes more rapid setting speed.

The PVOH-protected emulsion and adhesives made with it spray very well in airless spray systems, but relatively poorly in air spray systems.

Table 4 further illustrates that the PVOH-protected and the cellulosic emulsion are both excellent bases for adhesives to bond to polyvinyl chloride. The PVOH-protected emulsion is usually chosen for wet laminations and the cellulosic emulsion for heat-seal applications.

The surfactant emulsion shows much better adhesion to polystyrene than the other two emulsions, but the other emulsions can be compounded with plasticizers and/or tackifier resins to make excellent polystyrene adhesive bases.

Though all three products exhibit the same glass transition temperature, the heat-seal temperature of the surfactant emulsion is below that of either the PVOH-protected or the cellulosic emulsions. Fig. 8 shows the difference between the PVOH-protected and the surfactant emulsion in laminating films of polyvinyl chloride to each other, using a heat-seal technique. In this case, each emulsion was coated onto a PVC film, allowed to dry, then heat sealed at the

**Table 4. How Protection System Affects the Properties of Three VAE Emulsions.**

<i>Property</i>	<i>Protection System</i>		
	<i>Polyvinyl Alcohol</i>	<i>Nonionic Surfactant</i>	<i>Surfactant and Cellulosic</i>
Borax compatibility	none	good	good
Dextrin compatibility	poor	good	good
Water resistance	good	excellent	very good
Water spotting	fair	excellent	good
Wet tack	excellent	poor	poor
Set speed	rapid	slower	slower
Sprayability	poor	excellent	excellent
PVC adhesion	excellent	fair	excellent
Polystyrene adhesion	fair	excellent	good
Heat sealability	good	fair	excellent
Thickening response	high	moderate	low
Solvent reactivation	good	fair	excellent
Compatibility with rubber Latices	fair	good	excellent

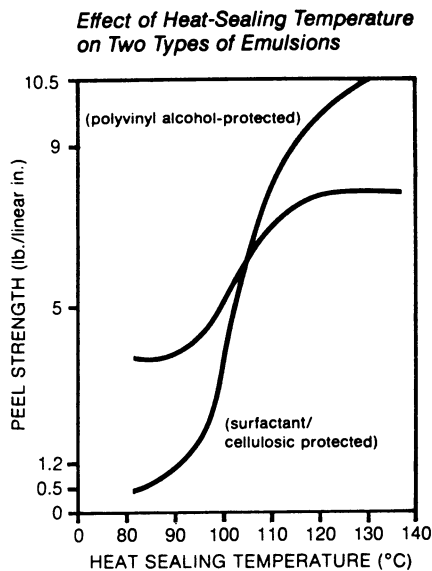
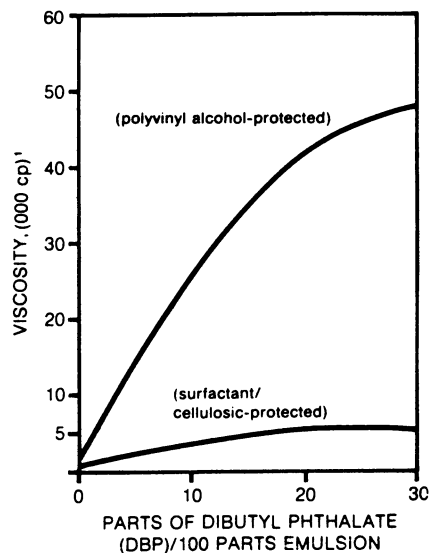


Fig. 8. Peel strength of PVC-to-PVC bonds.

temperatures shown on the horizontal axis. The laminations were then separated on an Instron® tester. The measured resistance to delamination is shown on the vertical axis of the chart. It should be noted that the emulsions can be blended to obtain intermediate adhesion values.

Plasticizer and solvent thickening response are other important compounding properties controlled by the protection system used in polymerization. Fig. 9 clearly shows that the polyvinyl alcohol-protected emulsion thickens much more rapidly than the surfactant and cellulosic-protected emulsions. The rapid thickening response of the PVOH-protected emulsion is an economic advantage in compounding many packaging adhesives. There are times, however, when it is necessary to have a high-solids, low-viscosity adhesive that contains high amounts of either plasticizer or solvent. The surfactant emulsion would then have an advantage over the PVOH-protected emulsion; but again, it is possible to blend these two emulsions to obtain intermediate properties.

The protection system used with polyvinyl acetate emulsions also affects solvent reactivation. Solvent reactivation describes the technique whereby dried adhesive films are wet with solvents in order to reactivate the adhe-



1. Brookfield Viscometer, Model RVF at 20 rpm, 25°C.

Fig. 9. Thickening response of two Airflex emulsions to plasticizer.

sive. This technique would be used if two non-porous surfaces were to be joined together and it was not possible to use heat to soften and reactivate the adhesive. In this situation, small amounts of solvent could be used to reactivate the adhesive, resulting in very low emissions. This technique would also take advantage of the much higher molecular weight, and therefore greater tensile strength, of an emulsion-polymerized adhesive resin compared with a solvent-polymerized resin.

### Advantages of Polyvinyl Alcohol Protection

As a protection system, polyvinyl alcohol confers unique properties on emulsions stabilized with it. Since polyvinyl alcohol enhances the adhesive properties of polyvinyl acetate to such a great degree, a majority of adhesive emulsions use this protection system. In addition to the advantages listed in Table 5, polyvinyl alcohol-protected emulsions are easily modified to reinforce specific adhesive properties. Importantly, the resulting compounds exhibit excellent stability.

**Table 5. Advantages of Polyvinyl Alcohol Protection**

Good machinability
Easy cleanup
Good wet tack
Rapid setting speed
Rapid thickening response
Good heat resistance
Low degree of blocking
Crosslinkability

## POLYMER STRUCTURE AND PROPERTIES

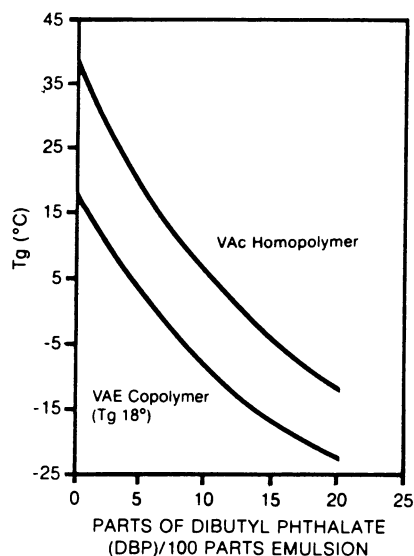
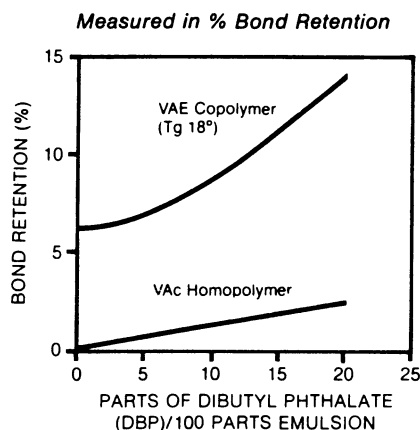
### Glass Transition Temperature

As indicated in Table 6, the glass transition temperature ( $T_g$ ) has notable effects on properties of adhesive emulsions. Varying the amount of ethylene incorporated into a copolymer has a direct relationship to the  $T_g$ : the more ethylene, the lower the  $T_g$ . The glass transition temperature affects such properties as flexibility, water resistance, PVC adhesion, paper adhesion, and setting speed. The three emulsions in Table 6 are all protected with polyvinyl alcohol. The major difference among them is the ethylene content as illustrated by the  $T_g$ . It should be noted that water resistance and ease-of-cleanup are inversely related.

The glass transition temperatures of polyvinyl acetate emulsions may be lowered further by adding a plasticizer such as dibutyl phthalate (Fig. 10). Plasticizer addition will, in turn, increase water resistance (Fig. 11).

### Branching

The linearity of a polyvinyl acetate resin can be controlled during the polymerization pro-

Fig. 10. Effect of plasticizer on  $T_g$  of two emulsion types.

1. Cloth to cloth bonds

Fig. 11. Effect of plasticizer on water resistance of two emulsion types.

**Table 6. Effect of  $T_g$  on the Properties of Three VAE Emulsions**

Property	$T_g$ (0°C)	$T_g$ (-20°C)	$T_g$ (-30°C)
Wt % $-\text{CH}_2-\text{CH}_2-$ (approx.)	17%	25%	31%
Water resistance	good	fair	poor
PVC adhesion	excellent	poor	poor
Paper adhesion	excellent	good	fair
(Clay-coated board)			
Setting speed	excellent	good	fair



cess. Conditions such as high temperature and high catalyst concentration can favor the formation of pendant or branched segments on the linear chain.<sup>29</sup> This branching will increase tensile strength and toughness of the polymer. It will also increase the heat resistance (creep resistance) and reduce the tackiness of the polymer's dried film. A branched polyvinyl acetate emulsion will accept greater amounts of polar and water-miscible solvent without breaking (destabilizing) than will a linear type. Some effects of branching and chain structure on adhesion have been reported.<sup>34</sup>

### Functional Groups

Polyvinyl acetate emulsions can be further modified by the incorporation of functional groups. These groups permit the design of polymers which have the ability to bond a wider spectrum of surfaces, including difficult-to-bond substrates. The addition of functional groups also permits crosslinkability of the polymer in order to achieve a high degree of water, solvent, or heat resistance.

*N-Methylolacrylamide* is commonly used to manufacture self-crosslinking vinyl acetate polymers.

Rigid polymers are available which can be used to make highly water resistant wood adhesives. Other copolymers are available which are flexible enough to be used as water or solvent resistant nonwoven binder or as flocking adhesives. The *N*-methylolacrylamide copolymer will usually require the addition of an acid salt and a heat cure to achieve the desired effect.

*Carboxyl* functionality in a vinyl acetate-ethylene emulsion offers three advantages over noncarboxylated products. They are; increased adhesion to metals and polymeric surfaces; reactive sites for crosslinking; and a means for thickening.

Carboxyl functionality increases the adhesion of vinyl acetate-ethylene to several metals (Table 7). A conventional vinyl acetate-ethylene and a carboxylated vinyl acetate-ethylene polymer both may have the same glass transition temperature and the same ratio of vinyl acetate to ethylene, but the carboxylated vinyl

**Table 7. Peel Strength<sup>a</sup> of Cloth-to-Metal Bonds<sup>b</sup> (lbs./linear in.)—Effect of Carboxyl Functionality on Vinyl Acetate-Ethylene Polymers**

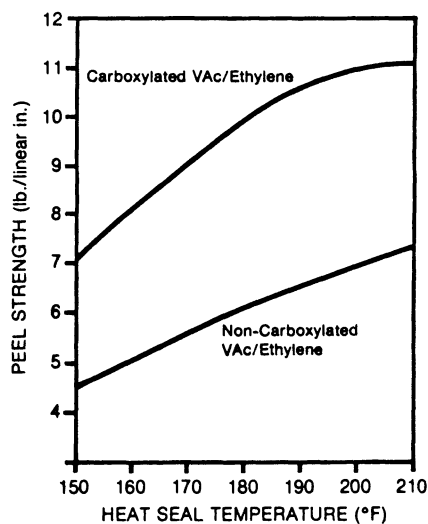
	Conventional Vinyl Acetate-Ethylene	Carboxylated Vinyl Acetate-Ethylene
Aluminum	0.4	1.8
Brass	0.8	4.5
Copper	0.6	3.9
Galvanized steel	0.6	3.5
Lead	0.7	1.4
Steel	1.3	4.1

<sup>a</sup>T Peel (180° peel on Instron® tester, 2 in./min).

<sup>b</sup>Cotton poplin cloth. Laminated wet. Dried 24 hours.

acetate-ethylene polymer adheres much better to metal substrates.

The incorporation of a carboxyl functionality reduces the softening range of vinyl acetate-ethylene resin while enhancing its adhesion. Fig. 12 shows the difference in adhesion between carboxylated vinyl acetate-ethylene and conventional vinyl acetate-ethylene polymer when each is used as a heat-seal adhesive for bonding two pieces of commercial polyvinyl chloride film. For test purposes, these emul-



1. Adhesion of PVC to PVC film; heat-sealed on a Sentinel Heat Sealer using constant pressure of 40 psi; 8 seconds dwell time.

Fig. 12. Effect of carboxyl functionality on heat-seal adhesion. Adhesion of PVC to PVC film. Heat sealed on a sentinel heat sealer using constant pressure of 40 psi; 8 seconds dwell time.

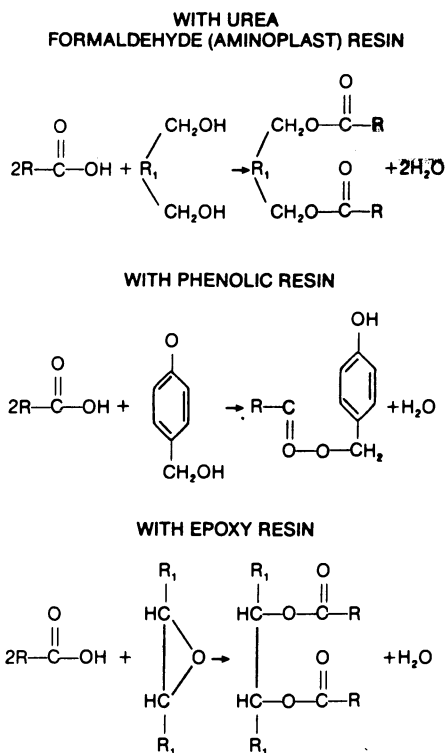


Fig. 13. Reactions of a carboxylated vinyl acetate-ethylene emulsion.

sions were coated on one piece of film, allowed to dry, and then heat-sealed to the uncoated PVC film. Carboxylated vinyl acetate-ethylene polymer will react with aminoplast, phenolic, and epoxy resins (Fig. 13). The reaction of the

carboxylated vinyl acetate-ethylene with aminoplast increases the polymer's water and creep resistance, especially when the bond is heat-cured (Table 8).

## COMPOUNDING

Many polyvinyl acetate emulsions can be used as adhesives without modification. However, an adhesive is usually compounded in order to tailor the product for a particular application. Compounding of adhesives facilitates application on equipment and bonding on specific substrates. It also imparts resistance to ambient conditions. In addition to film formers, an adhesive usually contains some of the following components; plasticizers, viscosity/rheology modifiers, tackifiers/extenders, solvents, fillers, humectants, surfactants, and biocides.

## Plasticizers

Copolymer emulsions are flexible and soft because of bulky pendant groups or flexible backbones. Polyvinyl acetate homopolymer emulsions series are hard and stiff due to the steric hindrance of the acetate groups and the strong intermolecular attraction. Any of these emulsion families may be compounded with plasticizers to increase flexibility.

Plasticizers are added to reduce the intermolecular attraction of the polyvinyl acetate polymers. They cause the polyvinyl acetate

**Table 8. How the Reaction of Carboxylated VAE Emulsion with Urea Formaldehyde (Aminoplast) Resin Affects Water and Creep Resistance.<sup>a</sup>**

Parts UF Resin	Peel Strength <sup>b</sup>		(lbs/linear inch)	
	Dry	Wet (uncured)	Wet (cured) <sup>c</sup>	Creep mm/min <sup>b</sup> (cured) <sup>c</sup>
0	13.0	3.0	5.8	0.96
3-Beetle 60	12.8	3.2	7.1	0.58
5-Beetle 60	12.6	3.4	7.4	0.23
10-Beetle 60	12.0	4.0	7.5	0.25
3-Beetle 65	12.0	2.9	8.3	0.36
5-Beetle 65	11.8	3.1	8.2	0.23
10-Beetle 65	11.0	3.6	7.9	0.01

Tests used cotton poplin to cotton poplin bonds. Cloth was laminated, then dried 7 days at room temperature.

<sup>a</sup>T Peel (180° peel on Instron® tester, 2 in./min).

<sup>b</sup>T Peel (500 g static load/linear/in., 170°F).

<sup>c</sup>Cured for 5 minutes at 275°F.

particles to swell; this raises the viscosity of the emulsion (Fig. 14) and destabilizes it for faster breaking and setting speeds. In addition, the resin particles in the emulsion gain mobility. Increased mobility helps the resin to wet smooth, nonporous surfaces, (e.g., films, foils, and coated papers) and consequently to increase its adhesion to these surfaces. Moreover, softened polymer particles coalesce more rapidly and more completely at lower temperatures.

When added to an emulsion, plasticizers will also lower the glass transition temperature ( $T_g$ ) of the polyvinyl acetate film, making it softer and more flexible (Fig. 15). Finally, plasticizers will increase the tackiness of the film, reduce its heat-sealing temperature, and improve its water resistance (Fig. 16).<sup>30,31</sup>

The general-purpose plasticizers listed in Table 9 can be added to polyvinyl acetate homopolymer and copolymer emulsions. Fire-retardant plasticizers, which are occasionally needed, are also listed.

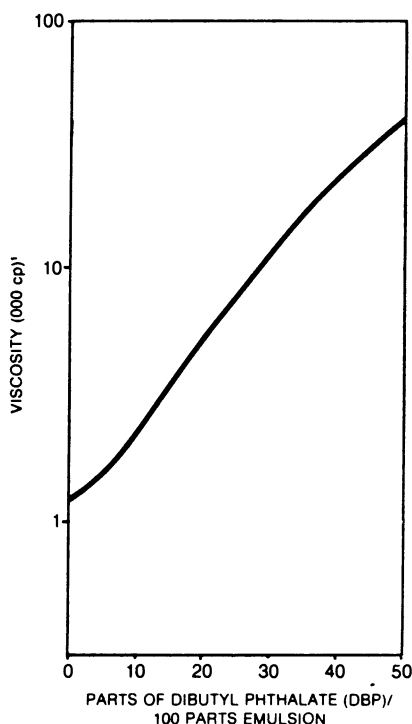


Fig. 14. Thickening response of homopolymer emulsion to plasticizers.

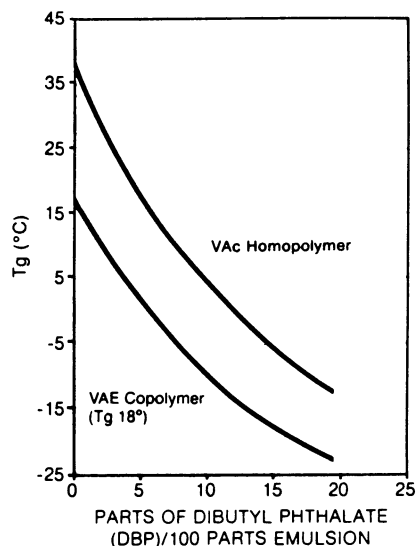


Fig. 15. Effect of plasticizer on  $T_g$  of two emulsion types.

### Viscosity/Rheology Modifiers

Adhesives are most commonly applied by machine. Each type of machine has its own viscosity/rheology requirements. Most roll applications use adhesives with a viscosity of 1500–3000 cp and operate best with a slightly thixotropic flow. Sprays require a more Newtonian flow and use viscosities in the 200–800 cp range. Construction adhesives are applied through a gun or trowel and use thixotropic or pseudoplastic, high viscosity materials. The proper choice of thickener will control viscosity as well as rheology.

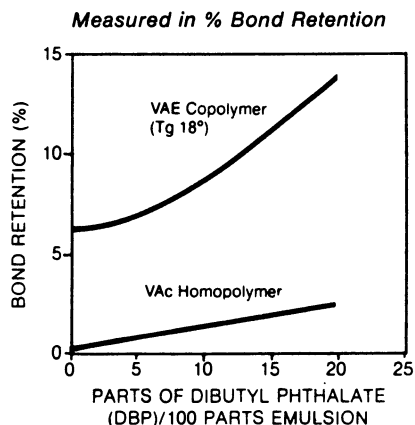


Fig. 16. Effect of plasticizer on water resistance of two emulsion types.

**Table 9. Plasticizers.**

<i>General Purpose</i>	<i>Fire Retardant</i>
Acetyl tributyl citrate	Cresyl diphenyl phosphate
*Butyl benzyl phthalate	
Butyl phthalyl butyl glycolate	*Tricresyl phosphate
	Triphenyl phosphate
*Dibutyl phthalate	
Dibutyl sebacate	
Diethyl phthalate	
*Diethylene glycol dibenzoate	
Dipropylene glycol	
*Dipropylene glycol dibenzoate	
Ethyl phthalyl ethyl glycolate	
Ethyl- <i>p</i> -toluene sulfonamide	
Hexylene glycol	
Methyl phthalyl ethyl glycolate	
Polyoxyethylene aryl ether	
Tributoxyethyl phthalate	

\*Denotes most frequently used.

Thickeners added to an adhesive will raise viscosity and permit dilution with water. This reduces the total solids of the adhesive and thus lowers its (wet) cost. Thickeners release water slowly, and when combined with lower solids, they also slow the setting (prolong open time) of the adhesive. Thickeners such as polyvinyl alcohol, starch, and hydroxyethyl cellulose will improve adhesion to porous substrates by reducing penetration of an emulsion into the substrate and decreasing the likelihood of a "starved joint."

Some thickeners can prevent adhesives from spitting and throwing during high-speed applications. They permit them to transfer cleanly and break short rather than draw to fibers. Polyvinyl alcohol is a good example of this type of thickener. Polyvinyl alcohol is also recommended for high speed roll application because it does not shear thin as do other thickeners. Some other specific effects of polyvinyl alcohol on emulsion adhesive properties have been reported.<sup>32</sup>

Pseudoplastic (shear thinning) adhesives can be prepared by adding polyacrylates such as sodium or ammonium polyacrylate. Starch, cel-

lulosic, and fumed silica will also confer pseudoplasticity.

Thickeners that can be added to all homopolymer and copolymer polyvinyl acetate adhesive emulsions include those shown in Table 10.

### Tackifiers/Extenders

Tackifiers increase the tackiness and the setting speed of adhesives. They increase tackiness by softening the polyvinyl acetate polymer, both in the wet and in the dry adhesive film. They accelerate setting speed by raising the total solids content of the emulsion. This action has the twofold result of "crowding" the aqueous phase and making the emulsion less mechanically stable.

Tackifier resins often increase the affinity of adhesives for specific surfaces such as plastics and metal foils. They also lower the softening and heat-sealing temperatures of adhesive films.

Tackifiers are insoluble in the continuous (water) phase of the emulsion and must be dissolved in organic solvents and/or plasticizer before they can be added.

By virtue of adding to the adhesive properties of the polyvinyl acetate emulsion, tackifiers are also extenders. (Most are too brittle to act as adhesives in their own right and need the toughness of polyvinyl acetate in order to function). By raising the total solids content of the emulsion, tackifiers accelerate the breaking and setting speeds and may reduce the cost of the adhesives to the extent that the active (polyvi-

**Table 10. Thickeners**

Alginates
Bentonite
Casein
Fumed silica
Guar gum
Gum tragacanth
*Hydroxyethylcellulose
Locust bean gum
*Methylcellulose
Polyacrylic acid salts (ammonium, potassium, sodium)
**Polyvinyl alcohol
*Sodium carboxymethyl cellulose
*Starches

nyl acetate) solids can be diluted by adding water.

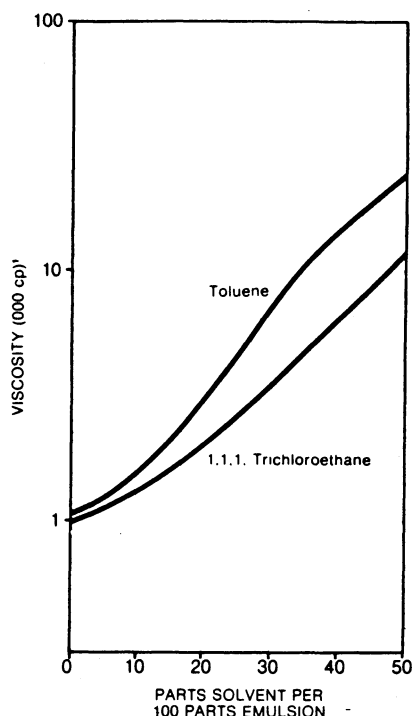
Plasticizers, solvents, tackified (borated) and untackified polyvinyl alcohol, and certain polyvinyl emulsions impart wet tack to polyvinyl acetate emulsions. Those additives specifically designated as tackifiers are listed in Table 11.

## Solvents

Because of their volatility, solvents perform like plasticizers on a temporary basis. Solvents increase the viscosity over that of emulsions; they also dissolve wax or resin coatings, accelerate setting speed, reduce film-forming temperature, reduce adhesive (wet) cost, increase wet tack, dissolve tackifiers, and lower the freezing point.

Like plasticizers, solvents cause the polyvinyl acetate particles to soften and swell, raising the viscosity of the emulsion (Fig. 17). Higher viscosity allows dilution of the adhesive with water, thus reducing the adhesive wet cost. Swelling and softening also destabilize the emulsion. This increases the setting speed and also allows the adhesive to coalesce into a film more rapidly and at a lower temperature than the neat emulsion. The improved coalescence results in greater water resistance for the film.

Low-boiling solvents impart only wet tack to the adhesive film, whereas high-boiling solvents confer both dry and wet tack and lower the heat sealing temperatures. High-boiling solvents behave like plasticizer except for eventual evaporation from the film. This evaporation aids wood glue or packaging adhesives that require fast setting speeds. Solvents can



1. Brookfield Viscometer, Model RVF at 20 rpm, 25°C

Fig. 17. Thickening response of homopolymer emulsion to two solvent types.

impart the necessary speed to the wet adhesive, but because they are volatile, will not cause the dried bond to creep.

Solvents promote adhesion to solvent-sensitive adherends (plastic films and reconstituted cellulose films) by swelling and partially dissolving them, thus allowing the adhesive to wet and/or penetrate the surface. Coated adherends that resist adhesion, such as printed, lacquered, or waxed papers, may also be partially dissolved by solvents to promote adhesion. (Chlorinated solvents are particularly effective on waxed surfaces).

Tackifier resins are usually dissolved in a solvent or a blend of solvent and plasticizer before being added to a polyvinyl acetate emulsion. The compounded solvent and resin has a crowding effect on the emulsion, which results in destabilization and a rapid setting speed.

The choice of solvents used with polyvinyl acetate homo and copolymer emulsions depends on the nature of the individual emulsion, and importantly, on the degree of branching of each emulsion. For instance, highly branched

Table 11. Tackifiers

*Coumarone-indene
Ester gum
Gum rosin
*Hydrocarbon resins
Hydrogenated rosin
Phenolic modified hydrocarbon resins
*Rosin esters
Tall oil rosins
Terpene phenolic
Terpene resins
Toluenesulfonamide-formaldehyde resin
Wood rosin

emulsions are more compatible with water-miscible solvents than other lesser-branched emulsions.

Table 12 classifies various solvent types as water-miscible or water-immiscible.

### Fillers

Fillers are added to emulsion adhesives to reduce cost by replacing resin solids without decreasing total solids, to reduce penetration into porous substrate, and to change the rheology of the compound. Depending on their individual properties, fillers can also add stiffness and strength or decrease tack and blocking. Un-

cooked starch fillers, in particular, reduce the cold flow in wood glues.

Clays and other fillers impart stiffness to adhesive films. Clays reduce the penetration of adhesives into porous substrates. Large-particle clays are better able to control penetration and also impart more rapid setting speed. A highly plastic clay, bentonite, makes adhesives thixotropic—fluid under high shear, thicker upon application. A study has been made<sup>31</sup> of the effect of various fillers on the adhesive properties of polyvinyl acetate.

Table 13 lists general purpose fillers than can be added to all polyvinyl acetate homo- and copolymer adhesive emulsions.

**Table 12. Water Miscibility of Various Solvent Types.**

<i>Solvents</i>	<i>Water Miscible</i>	<i>Water Immiscible</i>
ALCOHOLS		
Ethanol	•	
*Isopropanol	•	
Methanol	•	
Chlorinated Compounds		
Ethylene dichloride		•
Methylene chloride		•
Perchloroethylene		•
*1,1,1-Trichlorethane		•
Trichloroethylene		•
Esters		
Ethyl acetate		•
Methyl acetate		•
<i>n</i> -Butyl acetate		•
Glycols, Ethers, and Oxides		
Diethylene glycol diethyl ether	•	
Diethylene glycol monobutyl ether	•	
Diethylene glycol monoethyl ether	•	
Diethylene glycol monomethyl ether	•	
Dioxane	•	
Ethylene glycol monoethyl ether	•	
Ethylene glycol monobutyl ether	•	
Lower glycol ethers	•	
Hydrocarbons		
Mineral spirits		•
Naphtha		•
*Toluene		•
Xylene		•
Ketones		
Acetone	•	
Cyclohexanone		•
Diacetone alcohol	•	
Isophorone		•
*Methyl ethyl ketone	•	
Methyl isobutyl ketone	•	
Miscellaneous		
Tetrahydrofuran		•

**Table 13. Fillers.**

Bentonite	Nut shell flours
*Calcium carbonate	Silica
Calcium silicate	Talc
*Clay	*Uncooked starches
Mica	Wood flour

### Humectants

A humectant is a hygroscopic substance, one that absorbs and retains moisture from the atmosphere. In emulsion adhesives, humectants prevent the surface of the compound from skinning by keeping it wet. When polyvinyl alcohol or starch is present, the humectant holds water, which plasticizes these materials and keeps them flexible after drying. By retarding drying, humectants also slow setting speed and extend the open time of the adhesive.

Humectants suitable for use in polyvinyl acetate homo and copolymer adhesive emulsions are shown in Table 14.

### Wetting Agents

The surface-active agents (surfactants) added to polyvinyl acetate form two classes: wetting agents and foam control agents.

Wetting agents aid the adhesive to wet the surface of the adherend, thereby improving adhesion. When a vinyl acetate-ethylene polymer is used to bond PVC, the secondary plasticizers in the film may exude to the surface, making the film very difficult to wet and bond. The addition of a good wetting agent ameliorates this situation.

Wetting agents help water penetrate the surface of an adherend. This allows the polymer particles to coalesce and set rapidly. These compounds also disperse solids throughout the adhesive, which reduce settling.

Many of the anionic wetting agents cause foaming if used to excess, and may also increase the water sensitivity of the adhesive film.

**Table 14. Humectants.**

Calcium chloride	Sodium nitrate
Diethylene glycol	Sorbitol
*Glycerine	*Sucrose
Hexylene glycol	*Urea
*Propylene glycol	

**Table 15. Wetting Agents.**

Alkylxyl polyether alcohols
Dodecyl benzene sodium sulfonate
Polyoxy ethylene sorbitan monooleate
*Sodium alkyl benzene sulfonate
*Sodium dioctylsulfosuccinate
Sodium tetradecyl sulfate
*Acetylenic glycols
Tetrasodium pyrophosphate

Therefore, these should be added in minimal amounts.

Wetting agents that can be used with polyvinyl acetate homo- and copolymer emulsions are listed in Table 15. The effect of various surfactants on PVAc latex film structure and properties has been studied.<sup>33</sup>

### Foam Control Agents

Foam control agents include antifoam and defoamer compounds. Foam causes problems in the manufacturing and the application of adhesives. Air in the formulation increases viscosity, which can be misleading when adding ingredients. A misleading viscosity also prevents accurate metering during application of the adhesive, thereby preventing the deposit of sufficient solids on the glue line.

A small amount of foam control agent, 0.1–0.2% of the adhesive, is usually sufficient to prevent or break foam.

A foam control agent should be pretested in each new adhesive formulation and each time an ingredient is changed. Changing the amount of an ingredient can change foam control requirements. The adhesive sample should age 6–8 weeks before analysis of foam control efficiency. Some foam controllers may emulsify or separate upon aging.

### Biocide

Biocides are required when animal or vegetable substances or their derivatives (starches, casein and other proteins, nut shell flours, sugar, and cellulosic resins) are incorporated into polyvinyl acetate homo- or copolymer emulsion adhesives. Growing microorganisms digest these substances and can generate foul odors, discolor the adhesive, lower its viscosity, and weaken the bond.

**Table 16. Recommended Modifiers—Trademarks and Suppliers.**

<i>Plasticizers</i>		<i>Thickeners</i>	
Abalyn®	Hercules Inc.	Natrosol®	Hercules
Hercoflex®	Hercules Inc.	Cellosize®	Union Carbide
Hercolyn®	Hercules Inc.	Methocel®	Dow Chemical
Benzoflex® 2-45, 9-88, 50	Velsicol Chemical Corp.	Polyco® 296W	Borden Chemical
Pycal® 95	ICI Americas	Polyoxy® WSRN 750	Union Carbide
Celluflex® CEF	Stauffer Chemicals	Carbopol®	BF Goodrich Chemical Co.
Resoflex® 296	Cambridge Industries		
Santicizer® 8, 160, M17, 140, 141	Monsanto		
<i>Tackifiers—Extensing Resins</i>		<i>Solvents</i>	
Hercolyn®	Hercules	Chlorothene®	Dow Chemical Co.
Polpale® Resin	Hercules	Cellosolve®	Union Carbide
Stabelite® Ester 3, 10	Hercules	Carbitol®	Union Carbide
Piccolite®	Hercules		
Piccoflex®	Hercules		
Piccolastic®	Hercules		
Piccopale®	Hercules		
Foral® 85	Hercules		
Vinsol®	Hercules		
Santolite® MS	Monsanto		
MHP, MS80			
Bakelite® CKM2400	Union Carbide		
Bakelite® CKM2432	Union Carbide		
Bakelite® CKR0036	Union Carbide		
Bakelite® CKR2103	Union Carbide		
Nevillac®	Neville Chemical Co.		
<i>Thickeners</i>		<i>Surfactants</i>	
Cabosil®	Cabot Corp.	Surfynol®	Air Products and Chemicals, Inc.
		Aerosol® OT	American Cyanamid
		Nopcowet® 50	W. R. Grace and Co.
		Foamaster® JMY	W. R. Grace and Co.
		Tween®	ICI Americas
		Colloid® 682, 770	Colloid Inc.
		Drew® 1/250	Drew Chemical Corp.
		<i>Preservatives</i>	
		Dowicide® A, G	Dow Chemical Corp.
		Dowicil® 75	Dow Chemical Corp.
		Proxcel® GXL	ICI Americas
		Merbac® 35	Merck and Co., Inc.
		Kathon® LX	Rohm and Haas

The inclusion of 0.1–0.2% of a biocide, based on the total wet weight of the formulation, prevents microbial growth. Nevertheless, microbes frequently adapt to a specific biocide and flourish. Biocides should be changed regularly to prevent this occurrence.

### Polyvinyl Alcohol

Polyvinyl alcohol, a first class adhesive in its own right, also serves as an excellent additive for modifying the properties of polyvinyl acetate emulsion adhesives. See Chapter 22 of this volume.

### TRADEMARKS AND SUPPLIERS

Table 16 lists the most commonly used modifiers listed by their brand names and respective manufacturers. These modifiers are classified by functional uses, such as plasticizer, tackifiers, thickeners, solvents, and preservatives.

The grade numbers indicated may not be exhaustive of all those available; however, these are the most highly recommended.

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# Poly(Vinyl Alcohol) for Adhesives

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Poly(vinyl alcohol) (PVOH) is a water-soluble synthetic resin. It is produced by the hydrolysis of poly(vinyl acetate); the theoretical monomer,  $\text{CH}_2=\text{CHOH}$ , does not exist. Discovery of PVOH was credited to German scientists W. O. Herrmann and W. Haehnel in 1924, and the polymer was commercially introduced into the United States in 1939.<sup>1</sup>

Poly(vinyl alcohol), also known as polyvinyl alcohol, is a dry solid and is available in granular or powdered form. Grades include both the fully hydrolyzed form on poly(vinyl acetate) and products containing residual, i.e., unhydrolyzed, acetate groups. Resin properties vary according to the molecular weight of the parent poly(vinyl acetate) and the degree of hydrolysis. A wide range of grades is offered by PVOH manufacturers.

The wide range of chemical and physical properties of PVOH resins has led to their broad industrial use. They are excellent adhesives and highly resistant to solvents, oil, and grease. Poly(vinyl alcohol) forms tough, clear films that have high tensile strength and abrasion resistance. Its oxygen-barrier qualities are superior to those of any known polymer; however, PVOH must be protected from moisture, which greatly increased its gas permeability.

Poly(vinyl alcohol) also contributes to emulsification and stabilization of aqueous dispersions.

The main uses of PVOH in the United States are in textile and paper sizing, adhesives, and emulsion polymerization. Significant volumes are also used in such diverse applications as joint cements for building construction, water-soluble film for hospital laundry bags, emulsifiers in cosmetics, temporary protective films to prevent scratching of highly polished surfaces, and soil binding to control erosion. Poly(vinyl alcohol) is an intermediate in the production of poly(vinyl butyral), the adhesive interlayer in laminated safety glass. Outside the United States, PVOH is also used for textile fiber, although it must be chemically treated to become water-insoluble.<sup>2</sup> Poly(vinyl alcohol) fiber is produced in Japan and the People's Republic of China for captive use.

## PHYSICAL PROPERTIES

The physical properties of PVOH are controlled by molecular weight and the degree of hydrolysis. The upper portion of Fig. 1 shows the variation in properties with molecular weight at a constant degree of hydrolysis.<sup>3</sup> Hy-

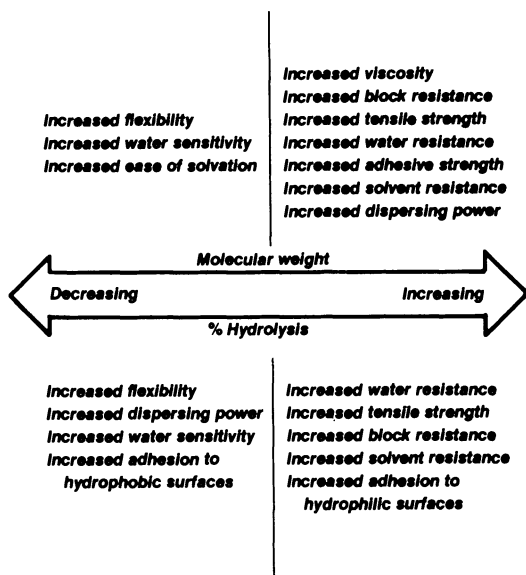


Fig. 1. Properties of poly(vinyl alcohol).

**Table 1. Physical Properties of Poly(Vinyl Alcohol).**

Property	Value
Appearance	
Specific gravity; of solid	White-to-cream granular powder 1.27-1.31
of 10 wt % solution at 25°C	1.02
Thermal stability	Gradual discoloration above 100°C; darkens rapidly above 150°C; rapid decomposition above 200°C
Refractive index (film) at 20°C	1.55
Thermal conductivity, W/(m · K) <sup>a</sup>	0.2
Electrical resistivity, ohm-cm	(3.1-3.8) × 10 <sup>7</sup>
Specific heat, J/(g · K) <sup>b</sup>	1.5
Melting point (unplasticized), °C	230 for fully hydrolyzed grades; 180-190 for partially hydrolyzed grades
T <sub>g</sub> , °C	75-85
Storage stability (solid)	Indefinite when protected from moisture
Flammability	Burns similarly to paper
Stability in sunlight	Excellent

<sup>a</sup>To convert W/(m · K) to (Btu · in.)/(h · ft<sup>2</sup> · °F), divide by 0.1441.

<sup>b</sup>To convert J to cal, divide by 4.184.

given in the lower portion of the figure. Since hydrolysis and molecular weight can be independently controlled in the manufacturing process, a product matrix has evolved that provides the property balance needed for different applications. The PVOH product matrix has four important molecular weight ranges and three key hydrolysis levels, although intermediate products are available (see Specifications). Various physical properties are listed in Table 1.

## SOLUBILITY

All commercial PVOH grades are soluble in water, the only practical solvent. The ease with which PVOH can be dissolved is controlled primarily by the degree of hydrolysis. Fig. 2 shows the effect of degree of hydrolysis on solubility with other variables held constant. Fully hydrolyzed products must be heated close to the atmospheric boiling point of water to dissolve completely. Lower temperatures are required as the degree of hydrolysis is decreased until 75-80% hydrolysis is reached, at which point

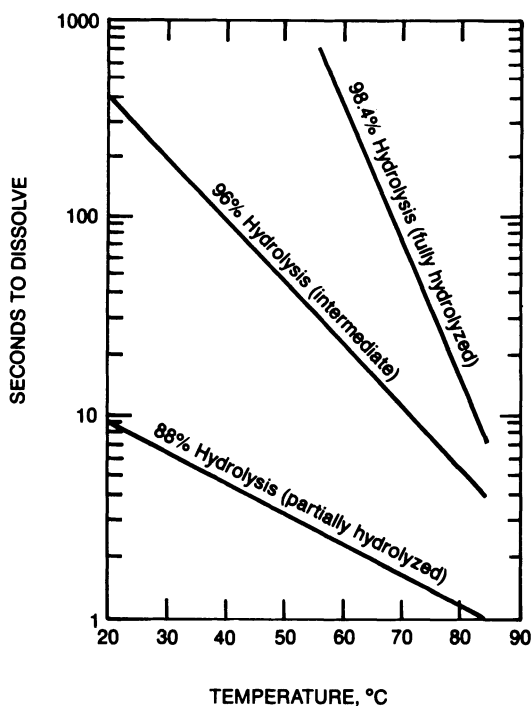


Fig. 2. Solubility of 0.4-mm poly(vinyl alcohol) cast film.

the product is fully cold-water soluble but precipitates upon heating. The hydrolysis range of 87–89% is considered optimum for both cold and hot water solubility. Products with this optimum degree of hydrolysis are commonly referred to as *partially hydrolyzed poly(vinyl alcohol)*. Regardless of the degree of hydrolysis, all commercial PVOH grades remain dissolved upon cooling.

Solubility is also influenced by particle size, i.e., surface area, molecular weight, and crystallinity. Decreasing particle size and molecular weight improves the solubility weight. Crystallinity is induced by heat treatment and retards the solubility rate.<sup>4</sup> Because the presence of residual acetate groups reduces the extent of crystallinity, low hydrolysis grades are much less sensitive to heat treatment.

Poly(vinyl alcohol) solutions show a high tolerance toward many electrolytes, as shown in Table 2. Small additions of strong inorganic acids and bases do not precipitate PVOH from solution, but the hydrolysis reaction continues to completion at extreme pH.

Poly(vinyl alcohol) cannot be dissolved by most common organic solvents, e.g., gasoline, kerosene, benzene, xylene, trichloroethylene, carbon tetrachloride, methanol, ethylene gly-

col, acetone, and methyl acetate.<sup>5</sup> It has limited solubility in dimethyl sulfoxide; the solubility is in proportion to the residual acetate content. Although there are no good solvents for PVOH other than water, up to 50% of lower alcohols can be added to PVOH solutions without causing precipitation.

## SOLUTION VISCOSITY

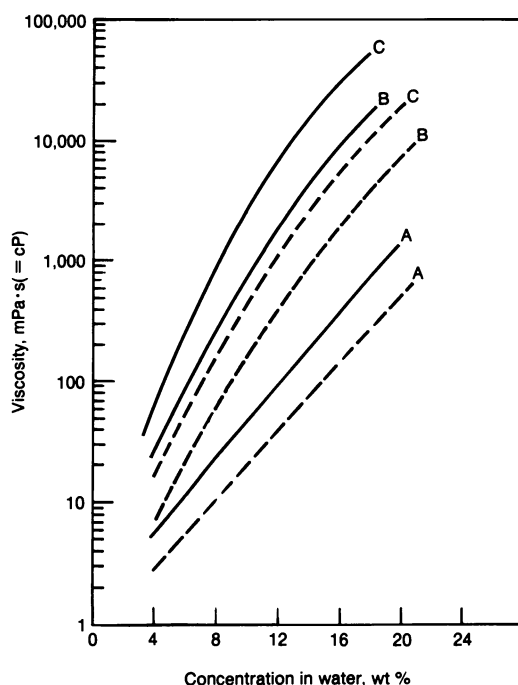
The viscosity of a PVOH solution is controlled by molecular weight, concentration, and to lesser degree, temperature. Degree of hydrolysis does not strongly affect viscosity, although the viscosity is proportional to degree of hydrolysis at constant molecular weight. Viscosity relationships for low, medium, and high molecular weight grades are shown in Fig. 3. Viscosity, rather than solubility, limits the concentration of PVOH solutions. With conventional batch-mixing equipment, the practical concentration limits for low, medium and high molecular weight resins are ca 30 wt %, 20 wt %, and 15 wt %, respectively.

**Table 2. Maximum Salt Concentration in which PVA is Soluble, % in Water.<sup>a,b</sup>**

Electrolyte	PVA degree of hydrolysis	
	95%	88%
Na <sub>2</sub> SO <sub>4</sub>	5	4
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	6	5
Na <sub>2</sub> HPO <sub>4</sub> · 7H <sub>2</sub> O	8	5
Na <sub>3</sub> PO <sub>4</sub> · 12H <sub>2</sub> O	8	6
Na <sub>2</sub> HPO <sub>4</sub> · H <sub>2</sub> O	9	6
NaHCO <sub>3</sub>	9	7
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> · 16H <sub>2</sub> O	10	6
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> · 5H <sub>2</sub> O	10	8
ZnSO <sub>4</sub> · 7H <sub>2</sub> O	13	10
NaCl; KCl	14	10
CuSO <sub>4</sub> · 5H <sub>2</sub> O	15	10
CH <sub>3</sub> COONa · 3H <sub>2</sub> O	23	15
NaNO <sub>3</sub>	24	20

<sup>a</sup>Courtesy of Air Products and Chemicals, Inc.

<sup>b</sup>Determined by adding a 10% solution of PVA dropwise to 50 ml of the salt solution at increasing concentration until precipitation is observed.



Degree of polymerization: A, 800; B, 2000; and C, 2400. Solid line, at 20°C; broken line, at 65°C.

Fig. 3. Solution viscosity of poly(vinyl alcohol).

The viscosities of partially hydrolyzed PVOH solutions remain stable if the solutions are stored at high temperatures over a wide range of concentrations. However, viscosities of concentrated solutions of fully hydrolyzed PVA gradually increase over a period of days when stored at room temperature, and gelation occurs in products that contains  $<1$  mol % acetate groups. This viscosity increase or gelation can be reversed by reheating.<sup>6</sup> Lower solution concentrations and lower degrees of hydrolysis eliminate viscosity instability associated with long-term solution storage.

## MANUFACTURE

All PVOH manufacture involves poly(vinyl acetate) as the starting material. The theoretical monomer, vinyl alcohol ( $\text{CH}_2=\text{CHOH}$ ), does not exist. Conversion of poly(vinyl acetate) to PVOH is generally accomplished by base-catalyzed methanolysis;<sup>10</sup> sodium hydroxide is the usual base.

Poly(vinyl acetate) polymerization is accomplished by conventional processes, e.g., solution, bulk, or emulsion polymerization. Solution polymerization is favored because the subsequent alcoholysis reaction requires solvent addition.<sup>10</sup> The polymerization step determines the ultimate molecular weight of the PVOH. Catalyst concentration, temperature, and solvent control the degree of polymerization; acetaldehyde is an effective chain-transfer agent. It is the agent commonly used.

The degree of hydrolysis of PVOH is controlled during the alcoholysis and is independent of molecular-weight control. Fully hydrolyzed PVOH is obtained if methanolysis is allowed to go to completion. The reaction can be terminated by neutralizing or removing the sodium hydroxide catalyst. The addition of small amounts of water to the reactants promotes saponification of poly(vinyl acetate), which consumes sodium hydroxide. The extent of hydrolysis is inversely proportional to the amount of water added. A disadvantage of water addition is an increase in byproduct sodium acetate, which is present as ash in all commercially available grades of PVOH. The alcoholysis reaction can be carried out in a highly agitated slurry process; a fine precipitate

forms as the poly(vinyl acetate) converts into PVOH. The product is then washed with methanol and is filtered and dried. A moving belt process allows the PVOH to form a gel and subsequently to be cut into granular form.<sup>11</sup>

The alcoholysis process yields methyl acetate as a byproduct. The methyl acetate can be used as a solvent or it can be processed to recover methanol and acetic acid. One such process involves mixing the methyl acetate with water and passing them through a cation-exchange resin to catalyze the hydrolysis reaction.<sup>10</sup>

Methanol recovered from this process can be totally recycled to the methanolysis step, and the acetic acid is sold as a byproduct.

## POLYVINYL ALCOHOL IN POLYVINYL ACETATE EMULSION ADHESIVES

Polyvinyl alcohol is a first-class adhesive in its own right. It also serves as an excellent additive for modifying the properties of polyvinyl acetate emulsion adhesives.

Polyvinyl alcohol adheres particularly well to cellulosic substrates such as wood or paper. Adding it to a polyvinyl acetate emulsion will increase the affinity as well as the tensile strength of the formulation.

Because it is a hydrophilic polymer, polyvinyl alcohol functions as a humectant to retard the loss of water from the formulation and prolong open time of the adhesive film. Wet tack is increased and can be enhanced further by adding tackified (borated) polyvinyl alcohols.

Polyvinyl alcohol is used as a thickener to increase viscosity and control the solids content. When a high viscosity but low solids formulation is needed, a small amount of a high viscosity polyvinyl alcohol should be added. When both high viscosity and high solids are desired, a medium viscosity grade should be added. All grades impart smooth flow from applicator reservoirs and shear resistance at high machine speeds. Polyvinyl alcohol affords the best means of balancing the viscosity and solids content of an emulsion adhesive.

Partially hydrolyzed polyvinyl alcohols increase the stability of emulsion adhesives by functioning as emulsifiers and protective colloids.<sup>8</sup> These alcohols increase water sensitiv-

ity of adhesive films, making them useful in emulsions designed for remoistenable adhesives or in those requiring easy clean up. Partially hydrolyzed resin types are also used to preemulsify organic solvent solutions before adding them to emulsions adhesives. Fully hydrolyzed polyvinyl alcohols, however, increase the water resistance of adhesive films, particularly the medium and high molecular weight grades.<sup>12</sup>

All polyvinyl alcohols improve the machinability of emulsion adhesives; spitting and throwing are reduced on high speed equipment. All types have surface-active properties that promote thorough wetting of roller applicators and adherends. Wetting and penetration into the adherend are improved by using polyvinyl alcohols with lower molecular weight and hydrolysis. Since polyvinyl alcohol has a higher melting point (200°C) than the emulsion to which it is being added, it raises the heat-sealing and blocking temperature of the film and increases its overall heat resistance. All polyvinyl alcohol resins facilitate the incorporation of water-immiscible substances into the formulation and stabilize the adhesive. In addition, solvent and oil resistance are increased and creep is decreased by polyvinyl alcohol.<sup>12</sup>

## CROSSLINKING

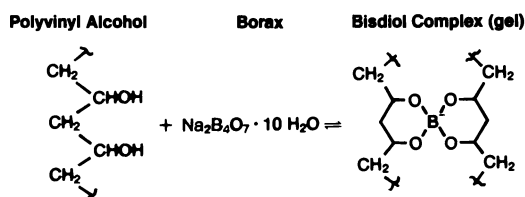
Poly(vinyl alcohol) can be readily crosslinked for improved water resistance.<sup>9</sup> The most practical means of crosslinking PVOH is with chemical additives, e.g., glyoxal, urea-formaldehydes, and melamine-formaldehyde. Trimethylolmelamine is often preferred if a low temperature is required. An acid catalyst, e.g., ammonium sulfate or ammonium chloride, is necessary with the formaldehyde crosslinkers. Metal compounds can also be effective insolubilizers for PVOH. These additives include strongly chelating metal salts of copper and nickel, e.g., cupric ammonium complexes, chromium complexes, organic titanates, and dichromates. The heat treatment during drying of PVOH films or coating is generally sufficient to complete the crosslinking reaction, although when dichromates are used the reaction is best catalyzed by ultraviolet light. Crosslinking slowly takes place even at room temperature,

and prolonged storage of the treated PVOH solution should be avoided. Crosslinking can also be accomplished by simply heating dry PVOH above 100°C; this dehydrates the polymer and yields an unsaturated carbon backbone. Intermolecular reactions between unsaturated groups in adjacent polymer chains form permanent crosslinks. However, thermal crosslinking is not considered a practical reaction because it is also accompanied by polymer decomposition.<sup>13</sup>

Although PVOH film can be rendered insoluble by crosslinking, it swells in water and loses strength upon extended exposure. Complete water insensitivity cannot be achieved, although it improves with degree of hydrolysis. Fiber-grade PVOH has a degree of hydrolysis of at least 99.9%; it exhibits negligible swelling in water, although it absorbs moisture, like many natural fibers.

## GELATION

The controlled gelation of PVOH solutions is important where penetration into a porous substrate is undesirable, e.g., paper coatings and adhesives. *Boric acid* and *borax* react strongly with PVOH and are widely used industrially as gelling agents. Poly(vinyl alcohol) is extremely sensitive to borax, which causes gelation by forming a bisdiol complex as shown below:



As little as 0.1% borax, based on solution weight, can cause thermally irreversible gelation. Boric acid forms a weaker monodiol complex and is preferred for controlled, partial gelation of PVOH.<sup>7</sup> The reaction is very sensitive to pH, and full gelation occurs above pH 6.

Boration causes aqueous solutions of PVOH to develop strong wet tack after cooking. Adhesives based on tackified (borated) poly(vinyl alcohol) work particularly well where they can be applied as a very thin film and then the sub-

strates mated using very high pressures. These conditions are found in spiral tube winding and solid fiber laminating. These adhesives are usually prepared at solid content levels of 18–25%. The poly(vinyl alcohol) content varies from 5 to 9%; the remainder of the solids is comprised of kaolin clay. The liquid adhesive is applied at rates of 40–45 grams per 1000 square meters, which results in a dry application of 8–12 grams per 1000 square feet.

The tackified polyvinyl alcohols, introduced in the early 1960s, rapidly replaced starch/urea formaldehyde adhesives in solid fiber laminating and dextrine, compounded polyvinyl acetate and sodium silicate adhesives in spiral tube winding. The new adhesives demonstrated superior adhesion over silicates and dextrines to a wide variety of paper substrates. These adhesives reduce warp in solid fiber laminating and shrinkage in spiral tubes because of the low adhesive application rate and, thus, low amount of water added to the laminations. The low application rate and low resin level also made these adhesives very economical.

Another advantage of these adhesives is that they permit rapid bond formation when applied properly. Tubes and board bound with fully or superhydrolyzed polyvinyl alcohol and clay adhesives also have excellent water resistance, and are used where the box or tube may be exposed to water for an extended period, as is the case with military packages and composite cans or dynamite tubes.

The adhesive properties of polyvinyl alcohol also appeared attractive for the manufacture of corrugated board. Adhesives based on the superhydrolyzed grades of tackified polyvinyl alcohol were demonstrated at both the single face and double backer sections of modern corrugated machines which were run at full speed. The board had strong dry bonds, high water resistance and showed excellent nonwarp properties. But while the polyvinyl alcohol adhesives were a technical success, they were unable to compete economically against starch adhesives.

## PRODUCTION

There are two producers of PVOH in the U.S., four in Japan, and several in Europe, where Hoechst is the dominant one.

The PVOH process is highly capital intensive, requiring separate facilities for polymerization, alcoholysis and recovery of acetic acid and methanol from the byproduct methyl acetate.

Some major producers and announced capacities:

	Capacity (thousand metric tons/yr)
U.S.	
Air Products and Chemicals, Inc.	48
duPont	60
Japan	
Kuraray	110
Nippon Goshei	50
Denka	25
Unitiken	25
Total Japan	210
Europe	
Hoechst	30
Taiwan	
Chang Chun	34

## SPECIFICATIONS AND REGULATIONS

Three important commercially available types of PVOH are distinguished by the mole percent residual acetate groups in the resin: fully hydrolyzed (1–2 mol % acetate), intermediately hydrolyzed (3–7 mol %), and partially hydrolyzed (10–15 mol %) PVOH. Poly(vinyl alcohol)s with other degrees of hydrolysis are produced, but collectively, they have a much smaller market share than any of the three principal grades. When no reference is made to the degree of hydrolysis in describing PVOH, it is generally assumed to be a fully hydrolyzed grade.

Poly(vinyl alcohol) is produced in four general molecular weight ranges, as shown in Table 3. Several other molecular weight resins are

**Table 3. Molecular Weight of Main Commercial Poly(Vinyl Alcohol) Grades.<sup>a</sup>**

Viscosity grade	Nominal $M_a$	4% solution viscosity, $\text{mPa} \cdot \text{s}$ ( $= \text{cP}$ ) <sup>b</sup>
Low	25,000	5–7
Intermediate	40,000	13–16
Medium	60,000	28–32
High	100,000	55–65

<sup>a</sup>Courtesy of Air Products and Chemicals, Inc.

<sup>b</sup>Measured at 20°C with Brookfield viscometer.

**Table 4. FDA Regulations Applicable to Poly(Vinyl Alcohol) as an Indirect Food Additive.**

<i>Regulation</i>	<i>Description</i>
181.30	Prior sanctioned substances used in manufacture of paper and paperboard products used in food packaging for fatty foods only
175.105	Adhesives, no limitations
176.170	Components of paper and paperboard in contact with aqueous and fatty foods, extractive limitations
176.180	Components of paper and paperboard in contact with dry food, no limitations
177.1200	Cellophane coating, no limitations
177.1670	Poly(vinyl alcohol) film
177.2260	Filters, resin-bonded where filter fiber is cellulose
177.2600	Filters, resin-bonded; extractables must be less than 0.08 mg/cm <sup>2</sup> (0.5 mg/sq. in.)
175.300	Resinous and polymeric coatings
175.320	Resinous and polymeric coatings for polyolefin films; net extractable less than 0.08 mg/cm <sup>2</sup> (0.5 mg/sq. in.)
177.2800	Textiles and textile fibers, for dry foods only
178.3910	Surface lubricants in the manufacture of metallic articles

produced, but they have only a minor market share. Industry practice expresses the molecular weight of a particular grade in terms of its 4% aqueous solution viscosity. Intermediate viscosities can be achieved by blending. Products of different degree of hydrolysis can also be blended to develop, e.g., intermediate solubility. Blended products have a broad distri-

bution in molecular weight and degree of hydrolysis, which may be undesirable in some applications.

FDA regulations applicable to the use of PVOH as an indirect food additive are listed in Table 4.

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# Polyolefin and Ethylene Copolymer-based Hot Melt Adhesives

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The adhesive industry in the U.S. has had a remarkably steady growth over the past 15 years. Hot melts, in particular, have grown steadily from 100 million pounds in 1970 to over 400 million pounds in 1985. The annual growth rate over this total period averages above 10%. It is rather obvious then that hot melt adhesives have been the major growth segment in the adhesive industry, with the aqueous and solvent-based products showing a decline. The growth rate for polyolefin and ethylene copolymer based hot melt adhesives has slowed down until currently it approximates the growth in GNP. Emphasis in the adhesive industry, however, is still largely centered on the hot melt products, in particular those based on new block copolymers. While it is obvious that in one sense the hot melt adhesive market is maturing, there are still many new opportunities opening up.

The rapid growth of hot melt adhesives was the result of several factors. First, they provided many advantages, e.g.:

- Rapid set time produces an increase in production rate.
- Hot melt dispensing is easy to automate.

- The elimination of solvent recovery or disposal costs.
- Elimination of hazardous chemicals (solvents).
- Smaller space requirements for both storage and use.
- Reduced maintenance and cleanup costs.
- Wide formulating latitude to meet cost and performance needs for a variety of end uses.

The ability to speed up packaging lines to achieve much greater productivity without increasing space requirements, by simply converting to hot melt adhesives from cold glues, was an economic bonus to many companies. Hot melt application equipment interchangeable with aqueous dispensers was developed by several companies, permitting relatively inexpensive conversions to the hot melt system.

The use of solvents to produce quick setting adhesives came under pressure as environmentalists pushed to reduce the amount of solvent being released into the atmosphere. This effort was felt by both the adhesive manufacturer and the user of the solvent-based adhesive. Hot melt adhesives were a logical alternative, since they are 100% solid systems containing no solvent, and have a very rapid set time.

While this chapter will deal only with poly-

\*Retired

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olefin and ethylene copolymer based hot melts, it should be pointed out that several other polymer compositions are used in hot melt adhesives. Many of these are in competition with the polyolefins.

Early hot melt adhesives were based on ethyl cellulose and animal or hide glues. These were later replaced by synthetic resins such as polyamides and ethylene-vinyl acetate copolymers. More recently a new class of compounds, referred to as *block copolymers* because of their unique chemical structure, have emerged. These latter compounds are copolymers of styrene and butadiene, isoprene, or ethylene-butylene which tend to widen the flexibility property range of hot melt adhesives. They probably represent the fastest growing segment of the hot melt adhesives market at the present time. Their primary application is in hot melt pressure sensitive adhesives. Polymers based on other than polyolefin resins are discussed in other chapters in this handbook.

The ethylene-vinyl acetate copolymers cover a wide range of compositions and melt indices, as shown in Fig. 1.

## ADHESIVE FORMULATION

The estimated distribution of polyolefin hot melt adhesives by type is shown in Fig. 2. The actual amount of polymer used is somewhat different for the three types of adhesives because the EVA adhesives are formulated with large quantities of tackifiers and/or extenders, such as petroleum and synthetic waxes. Relative proportions of polymer in the various types of hot melt adhesives are estimated as shown in Fig. 3. This situation is expected to change during the next ten years as new polymers are developed to act as adhesives for specific end-use application.

A typical ethylene-vinyl acetate based hot melt is composed mainly of three components: (1) a polymer, 30–40%; (2) a modifying or tackifying resin, 30–40%, and (3) a petroleum wax, 20–30%. The quantity and relative amount of each material is governed by the performance requirements of the adhesive. The polymer forms the backbone of the adhesive, providing strength and toughness. The modi-

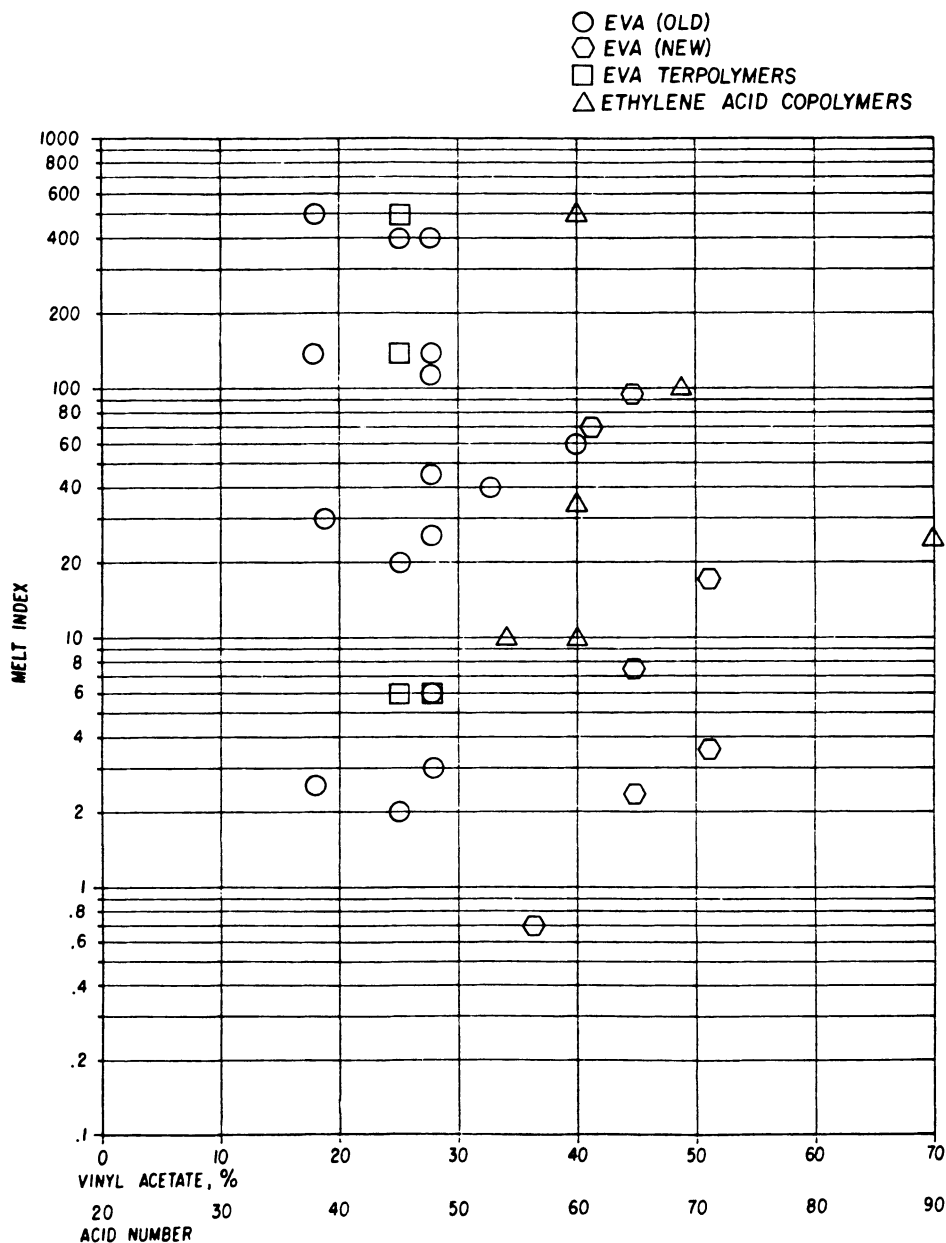
fying resin contributes surface wetting and tack, while petroleum wax is used to lower melt viscosity, reduce cost, and control setting speed. Antioxidants, fillers, plasticizers and blowing agents can also be used to enhance certain properties.

## Polymers

The large production capacity for ethylene and vinyl acetate monomers during the 1960s and early 1970s made ethylene-vinyl acetate resins with 18–40% vinyl acetate content readily available. In fact, with the exception of the period of the oil embargo in 1974–1976, when prices escalated rapidly, the polyolefin resins such as low molecular weight polyethylene, ethylene copolymers, and polypropylene resins took on the characteristics of commodity products. Each of these polymers is used extensively in producing hot melt adhesives. The ethylene-vinyl acetates were the most popular because of their superior adhesion to most substrates and their ease of formulation. Thus, EVA-based hot melt adhesives were developed for a wide variety of end-use applications. Low molecular weight polyethylene resins found their widest use in packaging applications with paper substrates, primarily paperboard cartons and corrugated containers.

Atactic polypropylene (APP) is tacky as produced and is not easily formulated. It is used essentially as a neat resin or extended with a small amount of wax or a polymer to add hot tack. Atactic polypropylene used to be a by-product in the production of crystalline polypropylene, but with the development of new, more efficient catalysts, less atactic polypropylene is produced. As a result, at least two companies are now producing APP directly. This means that a greater number of precise products are available; however, pricewise they will have to bear the full cost of production. It is therefore anticipated that atactic polypropylene resins will be developed mainly for specific applications having higher value-added performance.

The properties of polyolefin polymers which make them desirable as the base for hot melt adhesives are determined largely by two fac-



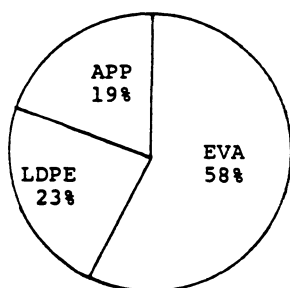


Fig. 2. Polyolefin melt adhesives by polymer type.

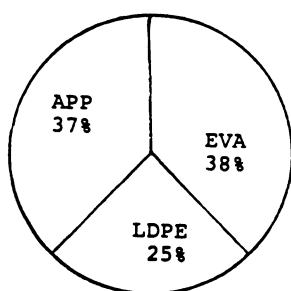


Fig. 3. Percent polymer distribution.

In Table 2 the property changes which can be expected by a change in melt index for ethylene-vinyl acetate copolymer are listed. It is followed by Table 3 showing the effects of vinyl acetate content on polymer properties.

The number of polymer suppliers continues to increase slowly as do the types of polymers. A listing of some of the polymer suppliers is given in Table 4. New polymers for hot melt

adhesive production are constantly being introduced as will be mentioned later.

### Tackifiers

Tackifiers are included in adhesive formulations to increase the adhesion of the polymer to various substrates. This is accomplished by facilitating the wetting of the substrate by reducing the viscosity of the hot melt. Besides the adhesive characteristics provided by the tackifier, its selection is also based on several physical properties such as color, heat, UV, and oxidation stability, and cost. The suitability of the resin is also largely dependent on its compatibility with other components of the adhesive blend, particularly the polymer.

Tackifiers tend to be grouped into three general categories: hydrocarbon resins, rosin esters and polyterpenes. There are numerous commercial products in each group, with over a hundred products available.

**Hydrocarbon Resins.** *C-5 aliphatic resins* are obtained as byproducts in the steam cracking of high naphtha or gas oils. They are largely composed of C-5 olefins, diolefins, and isoprene monomers. Typical producers of these compounds are Goodyear Tire and Rubber, Eastman Chemical, Arizona Chemical, Hercules, and Exxon Chemical. These resins have good color and hot strength and have good aging and heat stability properties. They are com-

**Table 1. Effect of Melt Index on Ethylene Homopolymer Adhesive Properties.**

High Melt Index 500	Improves heat seal strength → ← Improves flexibility ← Improves low temperature performance Improves hot tack → Increases melt viscosity →	Low Melt Index 2.0
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**Table 2. Effect of EVA Polymer Melt Index on Adhesive Performance.**

High melt Index 500	Improves heat seal strength → Improves flexibility → Improves hot tack → ← Improves low temperature performance Improves cohesive strength → ← Decreases melt viscosity Decreases open time →	Low melt Index 2.0
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**Table 3. Effect of EVA Polymer–Vinyl Acetate Content on Adhesive Properties.**

Lower vinyl acetate content 9%	Increases solubility → Improves flexibility → ← Higher seal strength ← Increases blocking resist ← Increases paraffin solubility Improves hot tack → Improves adhesion → Improves low temperature performance →	Higher vinyl acetate content 60%
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**Table 4. Polyolefin Polymer Suppliers for Hot Melt Adhesive Applications.****Polyethylene Homopolymers**

Eastman Chemical Products  
 USI Chemicals Co.  
 Union Carbide Corp.  
 Exxon Chemical

**Ethylene–Vinyl Acetate Copolymers**

E.I. duPont de Nemours & Co., Inc.  
 USI Chemicals Co.  
 Union Carbide Corp.  
 Exxon Chemicals

**Other Olefin Copolymers and Terpolymers**

Ethylene–ethyl acrylate: UCC, Dow Chemical, DuPont  
 Ethylene–acrylic acid: Dow Chemical  
 Ethylene–methacrylic acid: DuPont  
 Ethylene–vinyl acetate–methacrylic acid: DuPont

patible with ethylene–vinyl acetate copolymer resins and with LMWPE resins, are low in cost, and promote good adhesion to paper substrates. As a result, they are used extensively in packaging hot melt adhesives. Recently Goodyear has introduced new grades of hydrocarbon resins, “Wingtack plus” and “Wingtack extra,” which have increasingly small amounts of aromaticity which increases their compatibility with EVA polymers, resulting in slightly higher tensile strength, elongation, and viscosity. Aging and color characteristics also seem to be improved. Examples are shown in Table 5.

*C-9 aromatic* resins are produced from by-product streams resulting from the cracking of gasoline and from ethylene and propylene production. They are primarily based on styrene, alkyl benzene, vinyl toluene, and indene. While these resins promote good adhesion and hot strength, they have poor initial color, heat sta-

bility, and aging properties. Examples of these products are Nevex 100 (Neville Chemicals) and Piccovar L60 (Hercules).

*Dimer-5 cycloaliphatic resins* tend to be somewhat unstable, but there are hydrogenated grades which are sufficiently stable to have commercial acceptance.

*Aromatic monomer resins* which are highly saturated and purified are light in color and have excellent heat, light and oxygen resistance. Some examples of these products are Kristalex and Piccotex resins (Hercules Chemicals).

**Rosin Esters.** Rosin-based tackifiers find continued use in hot melt adhesives because of their unique property of providing compatibility to a wide variety of adhesive components. Thus, by including them among the ingredients the formulating latitude of the adhesive is greatly increased. However, they have lost ground to the C-5 hydrogenated resins because of their higher cost and uncertain supply.

Three types of rosins are available, differentiated by the source of the material. *Gum rosin* is derived from living pine trees, *wood rosins* from aged pine stumps, and *tall oil rosin* as a byproduct of the paper industry. Tall oil rosin has the largest source of supply, but it varies with the changing fortunes of the paper industry.

Unmodified rosins from all sources are highly unsaturated because their main constituent is abietic acid, which contains a conjugated double bond. Thus they are subject to degradation by oxygen, UV light, and heat. Therefore, the natural rosins must be modified to meet the stability requirements of the hot adhesives. Improved stability can be developed by several

**Table 5. Effect of Aromaticity on Hydrocarbon Resin.<sup>a</sup>**

<i>Ingredients</i>	<i>Wingtack 95</i>	<i>Wingtack Plus</i>	<i>Wingtack Extra</i>
Elvax® 350	30	30	30
Parafint H-1	20	20	20
Wingtack	50	50	50
<i>Properties</i>			
Tensile strength, psi	605	610	660
Elongation, %	50	110	265
Brookfield Viscosity, 300°F	5400	5600	6200
Color, aged 5 hrs @ 350°F	9.5	8.0	5.5

<sup>a</sup>ASC 1985, p. 16, Leonard J. Kuma, Goodyear Tire and Rubber.

processes such as hydrogenation, disproportionation, and dimerization followed by esterification of the rosin with glycerol or pentaerythritol. The modified rosins exhibit good adhesion, initial color, heat stability, and aging characteristics.

Terpene-based resins are obtained from turpentine sulfate, a byproduct of the paper industry, and from limonene, a product of the citrus industry. Products obtained are alpha-pinene, beta-pinene, and dipentene. The alpha-pinenes are apparently the preferred product for hot melt adhesives as they are the most compatible with EVA copolymers. Adhesives compounded with dipentenenes have excellent color and thermal stability, odor, oxidation resistance and hot tack properties. Typical of the products available in this class are the Piccolyte series of resins (Hercules). Limonene-based products are exemplified by Zonatac 105 (Arizona Chemicals).

It can be anticipated that other tackifying resins will be introduced as new products are developed. For example, Lawter International recently introduced a styrene/isobutylene resin containing a saturated polymer backbone which contributes improved heat and UV stability. These optically clear, low molecular weight, high styrene content polymers can be expected to provide another dimension for the adhesive chemist to improve the versatility of hot melt adhesives. Other examples are Amoco's alpha-methylstyrene and polybutenes. The latter are intermediate-to-low molecular weight homopolymers offering attractive properties including chemical stability, clarity, and resistance to oxidation by heat and light.

## Waxes

Waxes are included in hot melt adhesive formulations for several reasons, two of which are to lower cost and to reduce viscosity. Properties affected by the wax content are blocking characteristics, softening point, and open time. The high melting microcrystalline waxes (m.p. 190–195°F) and synthetic waxes (m.p. 210–245°F) are used because they contribute to high temperature properties and greater cohesive strength. The higher melting paraffin waxes (m.p. 150–160°F) are used extensively in hot melt coatings for their barrier, antiblocking and heat seal properties as well as their lower cost.

Waxes are generally included in hot melt adhesive formulations at the 20–30% level, but this concentration may drop in the future. Waxes have become considerably more expensive as refineries choose to lower their production of these products. Also, synthetic waxes produced by polyethylene producers are being structured to provide similar properties. Furthermore, as the polymer manufacturers modify their products to do the complete adhesive job, fewer and fewer additives will be required in the adhesive formulation.

## HOT MELT ADHESIVES APPLICATIONS

The fact that hot melt adhesives are the fastest growing type of adhesive means they are finding wide utility in literally thousands of individual applications. For convenience, these applications have been listed in twelve categories, as shown in Table 6.

**Table 6. Major Hot Melt Adhesive Applications.**

<i>Application</i>	<i>MM lb<sup>a</sup></i>
Case, carton, trays	116
Paper laminates	60
Nonwoven	50
Bookbinding	44
Labels	24
PET bottles	18
Bags	18
Textiles	15
Carpet seaming	12
Furniture	11
Cans, tubes, drums	4
Other	30
Total	400 plus

<sup>a</sup>Estimated 1985.

Packaging containers such as cases, cartons, and trays, both manufacture and closure, are the largest application for hot melt adhesives, representing about 25% of the total market. If all packaging applications are included, such as labels, bags, tubes, and cores, approximately 60% of hot melt adhesives are used in packaging. The other major uses of hot melt adhesives are in bookbinding, product assembly and nonwoven products, and paper laminates. Although the term *hot melt adhesive* is used for many applications, the actual formulation of the adhesive varies somewhat from end use to end use. The principal types of adhesive used in each of the categories are discussed next.

### Cases, Cartons, and Trays

This segment of the packaging market represents the largest application for hot melt adhesives—approximately 25% (excluding pressure sensitive adhesives). Of all the types of hot melt adhesives, polyolefins, as represented by EVA copolymers and low molecular weight polyethylenes, dominate this market. The EVA copolymer resins probably have 65% of the market, with low molecular weight polyethylenes at 30%. The EVA hot melt adhesives hold the largest share because of their ease of preparation, versatility, and widespread availability. As more sources of low molecular weight polyethylene and low density polyethylene resins become available at lower prices, EVA resins may lose some market share.

It should also be noted that water-based polyvinyl acetate and dextrin adhesives have been replaced by hot melt adhesives, which now have over 50% of the market. The reasons for the high rate of penetration are typical of those mentioned earlier for hot melts in general. But the increased speed and ease of automation are the primary ones.

Case sealing adhesives based on EVA resins are often a blend of several ingredients. A typical formulation is listed in Table 7.

A representative hot melt adhesive formulation based on a low molecular weight polyethylene resin would be composed of the materials shown in Table 8. A low density polyethylene based hot melt adhesive for case sealing might contain the formulation shown in Table 9.

This market is projected to grow roughly in step with the growth in GNP. Changes in formulation composition should be slightly in fa-

**Table 7. Hot Melt Case Sealing Adhesive.**

<i>Ingredients</i>	<i>Parts by Weight</i>
Elvax® 420 EVA polymer <sup>a</sup>	34
Shellwax 300 <sup>b</sup>	33
Zonatac 105 <sup>c</sup>	33
BHT (butylated hydroxytoluene)	0.2

<sup>a</sup>DuPont Company.

<sup>b</sup>Shell Chemical.

<sup>c</sup>Arizona Chemical Company.

**Table 8. LMWPE Case Sealing Adhesive.**

<i>Ingredients</i>	<i>Parts by Weight</i>
Epolene C-10 <sup>a</sup>	65
Atactic polypropylene <sup>a</sup>	10
Eastorez H-100 <sup>a</sup>	25
BHT (butylated hydroxy toluene)	0.2

<sup>a</sup>Eastman Chemical.

**Table 9. LDPE Hot Melt Adhesive.**

<i>Ingredients</i>	<i>Parts by Weight</i>
Petrothene NA593 <sup>a</sup>	40
Piccotac 95 <sup>b</sup>	40
Microwax, 185°F MP	20
BHT	1

<sup>a</sup>USI Chemicals

<sup>b</sup>Hercules, Inc.

vor of low density polyethylene. The largest change will probably be in the polymers themselves to make them more effective on an individual basis and thus reduce the amount of other components.

### Bookbinding

The use of hot melt adhesives in the construction of books and periodicals has grown very rapidly during the past ten years. This has been brought about by two developments. First is the tremendous increase in the production of lower cost paperback books. Paperbacks now constitute a major portion of all fiction and nonfiction books. Simultaneous with this phenomenon was the development of the "perfect binding" process. This process changed the method of manufacturing books from stapling and sewing to glueing of the pages at the spine or back of the book. Hot melt adhesives were ideal for this process and thus took over the market. Essentially all paperback books are constructed with hot melt adhesives. The use of these adhesives has now spread to the production of catalogs, telephone books, and many trade and consumer publications. Because of the greater adhesion and flexibility of EVA based hot melts, EVA resins have been used almost exclusively in this application. A typical bookbinding adhesive might be formulated as in Table 10.

Since paperback books are constructed essentially 100% with hot melts, future growth of hot melt adhesive production will be related directly to growth in paperback book sales. However, there is now the prospect that hard-

cover books may become a market opportunity. A large segment of this market has resisted hot melt penetration because of the nature of the books. The major outlet for these books is in school textbooks where continued use and long life are important. Also, the book is expected to be opened on a desk and to remain open. This reveals one of the disadvantages of polyolefin-based hot melt adhesives in that they exhibit *memory*. This characteristic causes the book to want to close rather than remain open. Some adhesive companies have now been able to formulate hot melt adhesives which are quite satisfactory in this regard. This development is the result of the more recent availability of the styrene-butadiene block copolymer resins. By introducing these resins into the hot melt adhesive formulation, adhesive flexibility is increased and memory reduced. This development has opened up the hardcover book market to hot melt adhesives. A representative hot melt adhesive utilizing block copolymer resins is illustrated in Table 11.

While the potential use of hot melt adhesives in hardcover books offers an opportunity for future growth, there are some limitations. The public is greatly concerned about the careless use of natural raw materials. Thus, the recovery and reuse of paper products is important. Hot melt adhesives, as currently compounded, are not easily redispersed as required in the repulping operation. One of the major current research goals is the production of hot melt adhesives which lend themselves to the repulping process. Limited success so far indicates this objective may ultimately be achieved.

**Table 10. Bookbinding Hot Melt Adhesive.**

<i>Ingredients</i>	<i>Parts by Weight</i>
Elvax® 260 EVA <sup>a</sup>	30-40
Rosin ester tackifier, R&B 100-105°C	25-45
F. R. Paraffin wax m.p. 150-160°F	15-30
White microcrystalline <sup>b</sup> wax, m.p. 180-190°F	5-10
Ethyl 330 antioxidant <sup>c</sup>	0.5

<sup>a</sup>DuPont Company.

<sup>b</sup>Bareco Div. Petrolite Corporation.

<sup>c</sup>Ethyl Corporation.

**Table 11. Bookbinding Adhesive Containing Styrene Block Copolymer.**

<i>Ingredients</i>	<i>Parts by Weight</i>
Elvax® 260 <sup>a</sup>	20-35
Kraton 1107 <sup>b</sup>	15-35
Foral 105 <sup>c</sup>	20-40
Shellflex 371 <sup>b</sup>	5-10
Microcrystalline wax, m.p. 170-190°F	10-15
Antioxidant (Irganox 1010) <sup>d</sup>	0.25

<sup>a</sup>DuPont Company.

<sup>b</sup>Shell Chemical Company.

<sup>c</sup>Hercules, Inc.

<sup>d</sup>Ciba-Geigy Corporation.



## Nonwovens

The nonwoven market includes such products as disposable diapers, sanitary products, incontinent diapers, hospital sheets and pads. Other products such as disposable caps and gowns and industrial throw-away garments are also included. The market for these products is expanding as new uses are constantly being developed, for example, in the field of filters and separators in the new biotechnology industry.

Nonwoven products are usually constructed of polyethylene and polypropylene materials which are very hard to adhere to. In spite of this, hot melt adhesives are used almost exclusively to bond most structures. Diapers represent the largest product line using hot melt adhesives. In the future it may be that incontinent diapers and absorbent pads will be an even larger market. EVA-based hot melts are believed to hold about 60% of the market, with low molecular weight polyethylene and atactic polypropylene making up the remainder. The type of adhesive used is constantly under change as the performance requirements change. The disposable diaper has penetrated approximately 80% of the total diaper market.

Hot melt adhesives used in diaper construction are of two general types: high viscosity systems based on atactic polypropylene for the end seal and lower viscosity, faster setting ethylene-vinyl acetate based adhesives for the side seam. With the evolution of the construction to a multi-line laminating system, manufacturers have adopted one or the other hot melt system with which they feel most comfortable. The composition of an atactic polypropylene based hot melt adhesive is illustrated in Table 12.

The side seam adhesive is presently undergoing some modification as new diaper configurations are being developed. More and more the

**Table 12. Atactic Polypropylene Hot Melt Adhesive.**

<i>Ingredient</i>	<i>Parts by Weight</i>
APP M5002 <sup>a</sup>	70
C-5 hydrocarbon resin	10
Microcrystalline wax	20

<sup>a</sup>Eastman Chemicals.

trend is toward form-fitting leg bands, which may be stretchable. This requires that the diaper adhesive both adhere to the polyolefin liner and be elastic or adhere to an elastic band inserted in the leg area. Both systems are used. An example of a general purpose EVA based adhesive is given in Table 13; an elastomeric adhesive formulation is given in Table 14.

The precise formulation of the adhesive is quite difficult, as the performance requirements are rather rigid. Tensile strength and heat resistance of the bond are important because the diaper must not come apart and release the fluff wadding, which might harm the child. The temperature/viscosity relationship of the adhesive must be controlled to permit easy application and surface wetting of the liner without puckering the liner material.

The nonwoven market is expected to continue to grow at a very rapid pace, at least 8% annually for the next several years; thus, it is an attractive market for hot melt adhesives.

## Furniture

In many of the hot melt adhesives markets the hot melt accounts for a large percentage of the adhesive used. This is not true of furniture. Furniture generally needs a rigid or structural adhesive, and this requirement is usually best met by a liquid adhesive, for example, a poly-

**Table 13. EVA Based Hot Melt Adhesive.**

<i>Ingredient</i>	<i>Parts by Weight</i>
Elvax® 220 <sup>a</sup>	30
Polyterpene resin	50
Microcrystalline wax, 185°	20
Antioxidant	0.5-1.0

<sup>a</sup>DuPont Company.

**Table 14. Elastomeric Adhesive.<sup>a</sup>**

<i>Ingredient</i>	<i>Parts by Weight</i>
Kraton SIS block copolymer <sup>b</sup>	20
Polyterpene tackifier <sup>c</sup>	60
Shell process oil <sup>b</sup>	10-20
Antioxidant	0.5-1.0

<sup>a</sup>National Starch Patent 4,526,577.<sup>1</sup>

<sup>b</sup>Shell Chemical Company.

<sup>c</sup>Union Camp.

vinyl acetate emulsion. As a result, hot melt adhesives compose only about 11% of the adhesive used in furniture construction. Hot melt adhesives are used in those areas where high strength is not usually required. EVA copolymer adhesives are used in low temperature laminations and in cabinet construction for drawer corner blocks, drawer bottoms, and molding applications for decorative effects. These adhesives are expected to continue growing as they replace the less stable and disappearing animal resin glues.

Hot melt adhesives are used in limited quantities in the lamination of plastic sheets to wood for doors and cabinets, although contact adhesives are generally chosen for this application. Edgebanding of veneered products is another application for hot melt adhesives, but polyamide hot melt adhesives are the preferred type because of their greater heat resistance.

A typical EVA hot melt furniture adhesive would be formulated as given in Table 15.

There are indications that the manufacture of laminated furniture will probably increase at a rate greater than GNP. Therefore, hot melt adhesives should have a good future in furniture applications, assuming some improvement in product performance. The main limitation of the current EVA adhesives is high temperature performance. But this may be improved by using carboxylated copolymers which have slightly higher temperature resistance.

A higher service temperature product assembly adhesive can be formulated by using an ethylene acid copolymer such as Elvax® II 5550. These adhesives approach the higher service temperature of polyamide adhesives, and thus are a low cost alternative in many applications. A typical formulation is shown in Table 16.

A more moderate temperature structural ad-

**Table 16. Hot Melt Product Assembly Adhesive.**

<i>Ingredient</i>	<i>Parts by Weight</i>
Elvax® II 5550 <sup>a</sup>	35
Foral AX <sup>b</sup>	64
Antioxidant	1
	100
<i>Properties</i>	
Brookfield Thermosel Viscosity at 350°F, cP,	9,500
Lap shear adhesion, psi:	
pine/pine	500
steel/steel	640
acrylic/acrylic	350
PVC/PVC	300
Lap shear failure, °C (°F)	82(180)

<sup>a</sup>DuPont Company.

<sup>b</sup>Hercules, Inc.

hesive as required in the manufacture of an automotive air filter can be prepared from the formula shown in Table 17.

## Labels

The label adhesive market consists essentially of two segments: non-pressure sensitive and pressure sensitive. Adhesives are used to adhere labels to glass, plastic and metal cans, and paper and film packaging. Hot melt adhesives are used in both of these categories to the extent of 40–50% of all types. This is also true within each category. This chapter will discuss only the non-pressure sensitive segment, leaving the other segment to be covered in Chapter 38.

Hot melt adhesives are usually applied to the label in advance. The adhesive is then reacti-

**Table 17. High Temperature Automotive Adhesive.**

<i>Ingredient</i>	<i>Parts by Weight</i>
Elvax® II 5640 resin <sup>a</sup>	40
Foral 105 rosin ester <sup>b</sup>	50
AC-8 polyethylene wax <sup>c</sup>	5
Shellflex 451 HP processing oil <sup>d</sup>	5
Antioxidant	0.25

<sup>a</sup>DuPont Company.

<sup>b</sup>Hercules, Inc.

<sup>c</sup>Allied Chemical Company.

<sup>d</sup>Shell Chemical.

**Table 15. Furniture Hot Melt Adhesive.**

<i>Ingredient</i>	<i>Parts by Weight</i>
Elvax® 420 <sup>a</sup>	40
Escorez 2101 hydrocarbon resin <sup>b</sup>	30
Escorez 1304 hydrocarbon resin <sup>b</sup>	10
Be Square 175 microwax <sup>c</sup>	20
Antioxidant	0.5

<sup>a</sup>DuPont Company.

<sup>b</sup>Exxon Chemical.

<sup>c</sup>Bareco Div., Petrolite Corporation.

vated by heating just before being applied to the substrate. Ethylene-vinyl acetate based hot melt adhesives have been used extensively in this market, but are expected to lose market share to adhesives containing styrene-butadiene block copolymers and the general shift of the overall market to pressure sensitive hot melt adhesives. The primary reason for the greater use of styrene block copolymers is their superior glue line flexibility, which is required in plastic bottle labels. The use of plastic bottles is expected to increase dramatically in the next few years. However, EVA polymer suppliers are working to overcome this deficiency by developing newer resins. An example of this is the DuPont Company's Elvax® 170, which is stated to have greater elastic properties, making it useful in the preparation of hot melt pressure sensitive adhesives. Perhaps the largest use of hot melt adhesives for labels has been for paper and plastic films used in meat packaging. Automatic machines for wrapping, weighing, and printing the label and then applying it to the package are in common use.

The future of hot melt adhesives in this market will depend on the shift to pressure sensitive labels. The increased use of plastic bottles and perhaps the need to recover the plastic material may change or dictate the adhesive composition. A typical hot melt label adhesive presently might have the general formulation shown in Table 18.

### Polyester Beverage Bottles

The use of polyester (PET) plastic bottles to replace glass bottles and cans as beverage containers has resulted in significant consumption of hot melt adhesives. The volume of PET bot-

tles, several billion annually, is still expected to grow at about 15% yearly over the next few years as they continue to replace cans and glass for many other products. The PET bottle requires a solid or flat base. At the present time this base is adhered to the plastic bottle by a hot melt adhesive. The rapid production of bottles requires a very rapid setting adhesive. Thus, hot melts have been the adhesive used from the beginning.

The future of this market does have some potential deterrents. Recovery of the plastic bottle will probably be required. The current method of recovery is to regrind the bottle. However, the base is composed of a different resin and thus must be removed. This is a costly step and suggests that in the future the bottle will be redesigned to eliminate the base. If and when this occurs, the amount and type of hot melt adhesive will be changed.

The hot melt adhesives are based on ethylene-vinyl acetate or ethyl acrylate copolymers or styrene block copolymers, because of the need to adhere to polyester. The starting point formulation for a PET bottle adhesive is given in Table 19.<sup>2</sup>

### Carpet Seaming Tape

The bonding together of carpet edges is an integral part of installing wall-to-wall carpeting. In the past, carpet segments were sewn together by a highly time-consuming process. Today, hot melt adhesive tapes are used by carpet installers to bond the carpet seams (edges) together, which results in the abutted edges appearing to be seamless. The seaming operation is done at the carpet installation site.

A strip of hot melt coated tape is placed on

**Table 18. Heat Activated Label Adhesive.<sup>a</sup>**

<i>Ingredient</i>	<i>Parts by Weight</i>
Elvax® 250 EVA <sup>b</sup>	25
Ultraflex wax <sup>a</sup>	32
Staybelite resin <sup>c</sup>	20
Cardipol LP 0-25 wax <sup>a</sup>	20
Armid C Amide <sup>d</sup>	2.5

<sup>a</sup>Petrolite Corporation, Bareco Division.

<sup>b</sup>DuPont Company.

<sup>c</sup>Hercules, Inc.

<sup>d</sup>Armak Industrial Chemicals.

**Table 19. Hot Melt PET Bottle Adhesive.**

<i>Ingredient</i>	<i>Parts by Weight</i>
Elvax® 210 (EVA copolymer) <sup>c</sup>	10
Kraton 1102 (SBS block copolymer) <sup>a</sup>	25
F.R. Paraffin Wax, m.p. 150°C	15
White mineral oil, U.S.P.	10
Sylvatac 95 <sup>b</sup>	40
Trinonylphenyl phosphite	0.15

<sup>a</sup>Shell Chemical Co.

<sup>b</sup>Arizona Chemical Co.

<sup>c</sup>DuPont Company

the floor, under the abutted carpet edges, with the adhesive coated side in contact with the carpet backing. The adhesive is activated by a specially designed hand-held heating iron. The two carpet edges are pressed down on the activated tape and joined directly under the iron. This system is so successful it is almost impossible to tell the carpet is composed of more than one piece.

Two types of hot melt adhesives are used in this application, which stresses high strength and shear resistance. Low molecular weight polyethylene based adhesive is exemplified by Eastman's Eastobond A-39. Competitive products are primarily based on ethylene-ethyl acrylate polymers. These ethylene-acrylate polymers are chosen because they give slightly higher shear strength performance than ethylene-vinyl acetate based products. A typical adhesive formulation is illustrated in Table 20.

### Paper Laminates

Paper laminating is a very large and diverse adhesive market. Paper, film, and foil laminations are a major part of the packaging market, and while hot melt adhesives are used in many of these applications, the largest outlet for hot melt adhesives is in the paper lamination for paper roll wrap and in the lamination for reinforced pressure sensitive tapes. In these applications, a high degree of shear strength is not required, and atactic polypropylene is a major component. In most cases the atactic polypropylene is used with very little additive. In the case of reinforced tapes it is usually coated onto the substrate paper or film, a scrim or matrix of glass or plastic fiber is embedded in the coating, and this is then combined with the second substrate. The laminated film is then coated

with a pressure sensitive adhesive to complete the product.

### HOT MELT APPLICATION EQUIPMENT

The continued rapid growth of the hot melt adhesive industry has challenged the equipment manufacturers. They have met the challenge quite effectively with diverse, dependable production equipment.

Hot melt adhesives are available as slugs (2–6 in.), pellets, pillows, and ropes as well as in drums. Slugs are used for small, intermittent application with hand operated or power-driven handguns. The adhesive rope handgun is useful for applying small amounts on a continuous basis. Automated packaging lines or other continuous-feed systems use pellets or other forms as a continuous feed to melt pots which supply the molten adhesive to the applicator head through heated lines. A number of available machines use drums, in which the adhesive is continuously melted and drawn off as it is used. This equipment is sometimes more effective than the melt pot, where the adhesive may change in viscosity with long heating, or, if it is overheated, may become charred.

The major types of continuous application equipment have been wheel coaters and glue line nozzles. Simplest is a grooved wheel which turns in a melted reservoir of glue. These have been highly refined to where the amount of adhesive is controlled by a doctor blade for quantitative application. A further refinement is the development of the print cylinder, where an internally mounted doctor blade allows a precise pattern to be printed on either flexible or rigid substrates. Patterns can vary from one inch to a width of 72 inches, and system can operate at speeds greater than 1,000 feet per minute.

The hand-held glue gun continues to receive many modifications as to nozzle size and versatility. Nozzles designed for specific applications have been produced where quantities warranted. These applications include electronic assembly, furniture, automotive, and appliance applications.

Equipment is now available which can supply several application nozzles from the one melt tank. Also, the efficiency of heated supply

**Table 20. Ethylene Ethylacrylate Based Hot Melt Adhesives.**

<i>Ingredient</i>	<i>Parts by Weight</i>
EEA (18% EA) <sup>a</sup>	30
Zonester 100 rosin ester <sup>b</sup>	30–40
Microcrystalline wax	40–30
Antioxidant	0.5

<sup>a</sup>Union Carbide Corporation.

<sup>b</sup>Arizona Chemical Company.

lines has been increased to such an extent that lines 50 feet long can be used.

Hot melt spray nozzles have been developed which permit the application of a uniform layer of adhesive, for example, in adhering textiles to foam substrates. This method is also particularly useful in bonding nonwovens.

The cost of using hot melt adhesives has been lowered by the introduction of foamed hot melt applicators. This system introduces an inert gas into the adhesive prior to the point of discharge. By using the adhesive foam the amount of adhesive applied can be reduced as much as 50%, thus significantly reducing the cost of the adhesive required. The foam system can also result in a thinner glue line, which is very advantageous in certain end uses.

There are many excellent manufacturers of equipment for application of hot melt adhesives and coating systems by many different ways in different physical forms. These include high and low pressure applicators, extruders, slot die coaters, roll coaters, pattern coaters, nozzles, wheels, guns, spray applicators, and foam applicators. The following are some of the major manufacturers of these types of equipment. No intent is made to exclude any manufacturer. However, in the interest of space the following are offered for consideration:

- Nordson Corporation, Amherst, OH 44001
- Meltex Corporation, Peachtree City, GA 30269
- Accumeter Laboratories, Marlborough, MA 01752
- Bolton-Emerson, Inc., Lawrence, MA 01842
- Grayco/LTI, Monterey, CA 93940
- Spraymation, Inc., Ft. Lauderdale, FL 33309

A more comprehensive listing may be obtained from the various trade and educational associations concerned with hot melt systems, which could provide information regarding manufacturers who are associated with their organizations.

## TRENDS IN NEW POLYMERS

The hot melt adhesive market for polyolefin based polymers has matured, but will continue

to expand slowly because of two factors: (1) the development of new markets and (2) the development of new polymers which will change the compositions. Specifically, the trend is to develop polymers which can be used as the principal component of the adhesives with only minor additions of other ingredients to provide specific properties. The driving force to bring this about is the nature of adhesive requirements in general. For example: an all purpose adhesive should be effective at temperatures of  $-40^{\circ}\text{F}$  to  $300^{\circ}\text{F}$ , with adhesion of 350–1,000 psi. These criteria cannot be met with the present polymers alone.

The extent of new polymer development is illustrated in Fig. 1. This chart shows the new polymers are extending the vinyl acetate content to higher levels, providing a wider range of molecular weight (melt index) and increasing the number of monomers. The early polymers contained mainly 18–28% combined vinyl acetate content. New EVA copolymers are now available at up to 50% VA content. During the 1960s and 1970s EVA resins with vinyl acetate contents of 9–33% were available, with those in the 25–28% range having the greatest utility for hot melt adhesives. The chart can now be expanded as new resins are made available. For example, 2 Elvax® 40W and 150 (DuPont) with higher vinyl acetate content and high MI provide hot melt adhesives with more open time and better adhesion to plastic and film substrates. Other new products are U.S.I.'s Vynathene 2902-30/35 with a melt index of 70. New resins are also being introduced which have high vinyl acetate content and low melt index. Typical of these products are Elvax® 170 (DuPont), with a vinyl acetate content of 35–37% and a melt index of 0.6–1.0; Vynathene (USI Chemicals) EY903, 45% vinyl acetate, melt index 7.5; EY904, 51% vinyl acetate, melt index 3.5; and EY905, 51% vinyl acetate with a melt index of 18. Resins with low melt index and high vinyl acetate content find application in hot melt pressure sensitive adhesives. Recently a new series of EVAs has been introduced with a small amount of an acid monomer. These ethylene-vinyl acetate-acid terpolymers produced by DuPont are particularly useful in promoting improved adhesion to polar and nonporous substrates and in increased toughness, flexibility and seal strength.

**Table 21. Ethylene/Vinylacetate/Acid Terpolymers.<sup>a</sup>**

<i>Grade</i>	<i>Melt Index</i>	<i>VA %</i>	<i>Acid No.<sup>b</sup></i>
Elvax® 4260	5-7	28	4-8
Elvax® 4310	420-580	25	4-8
Elvax® 4320	125-175	25	4-8
Elvax® 4355	5-7	25	4-8

<sup>a</sup>DuPont Company.<sup>b</sup>Acid number is the milligrams of potassium hydroxide required to neutralize one gram of polymer.

Examples of these products are listed in Table 21.

New ethylene copolymers have also been introduced such as the ethylene-ethyl acrylates promoted by Union Carbide and Dow Chemical. These have been followed by ethylene-acrylic acid copolymers. Acceptance of these polymers has been limited to specific applications, probably because of their higher cost.

Recently another series of ethylene copolymers has emerged in the marketplace. They include a series of ethylene-methacrylic acid copolymers introduced by DuPont under the trade name Elvax® II. These products are designed for high performance hot melt adhesives. They are high molecular weight copolymers with high acid functionality and outstanding thermal stability. Besides improving the normal properties associated with ethylene-vinyl acetate copolymers, these polymers also promote adhesion to glass and metals, have improved alkaline redispersibility and substrate wetting. Examples of these new polymers are given in Table 22.

Dow Chemical has introduced a somewhat similar series of polymers under the Primacor trade name.

As mentioned earlier, new polymers are being introduced to provide functionality for hot melt pressure sensitive adhesives. The first of these were Shell Chemical's styrene-butadiene and styrene-isoprene block copolymers,

which provide the flexibility and tack required at low temperature. Recently DuPont introduced a segmented ethylene-vinyl acetate polymer which has more elastic properties than conventional EVA copolymers. This product, Elvax® 170, gives the adhesive compounder another raw material with which to compete in the hot melt pressure sensitive adhesive market.

Atactic polypropylene still finds use in paper laminates and reinforced tape, but these markets are considered mature. Some research work is currently underway to produce polypropylene copolymers which will exhibit unusual properties. New polyamide and polyester resins, as well as more complex polymers, as polyamide-polyethers or polyester-polyethers, are also under development.

## FUTURE OF HOT MELT ADHESIVES

The future of hot melt adhesives will depend to a large extent on the ability of the polymer suppliers and adhesive compounders to create adhesives which will meet the ever-changing requirements dictated by new manufacturing processes and materials of construction. Hot melt adhesives have provided a new method of using adhesives without organic solvents or water. However, one of the main limitations of hot melt adhesives is their lack of high temper-

**Table 22. Elvax® II<sup>a</sup> Ethylene Acid Copolymers.**

<i>Grade</i>	<i>Melt Index</i>	<i>Acid No.</i>
5550	10	54
5610	500	60
5640	35	60
5650	10	60
5720	100	66
5950	25	90

<sup>a</sup>DuPont Company.**Table 23. Hot Melt Electron Beam Curable Adhesive.<sup>a</sup>**

<i>Ingredient</i>	<i>Parts by Weight</i>
Kraton D132OX <sup>b</sup>	50
Wingtack 95 <sup>c</sup>	45
Adtac 10 <sup>d</sup>	5
Phenolic antioxidant	1-2

<sup>a</sup>J. R. Erickson, Shell Development Co., Houston, Texas, *Adhesive Age*, April 1986, p. 22.<sup>b</sup>Shell Chemical.<sup>c</sup>Goodyear Tire and Rubber Company.<sup>d</sup>Hercules, Inc.

**Table 24. Adhesive Properties.**

<i>Properties</i>	<i>Before EB</i>	<i>After EB (5 mrad)</i>
Rolling ball tack, cm	1.2	1.8
Polyken Probe tack, kg	1.2	1.4
180° peel, pli	5.0	5.6
Holding power—kraft, min	2400A	>4,000
Holding power—steel, min	>4,000	3,500C
95°C Holding power—Mylar, min	91C	>1,000
Peel temperature limit, °C	111	>200

ature resistance. A method of overcoming this deficiency would significantly increase the utility of hot melt adhesives. Recently J. R. Erickson has reported on such a method which employs a new polystyrene-polyisoprene-poly-styrene block copolymer which can be formulated into a hot melt adhesive. This adhesive can then be cured by treatment with an electronic beam. Optimization of the rubber-type polymer and formulating experience should lead to an adhesive with properties unique from the present types.

A typical formulation is shown in Table 23, and a list of properties before and after radiation is given in Table 24.

The trend in new hot melt adhesives will be to develop more specific adhesives. Thus, the number and range of adhesives should increase. An example of a specialized adhesive is the development of a film heat-activated adhesive. The adhesive film may be 5–20 mils thick and can be cut to a variety of shapes for application. The adhesive is then activated by heat or other means such as radio frequency vibration.

Another example of the type of innovation taking place in the hot melt adhesive industry is given by Nicolmelt. They have devised a hot melt diaper adhesive that changes from a light yellow color to a bright blue when it gets wet, thus indicating the diaper needs replacing. Mothers should appreciate this and it should also increase the sale of diapers by promoting more frequent changes.

Numerous new polymer and adhesive compositions are being evaluated, as indicated by the number of new patents being issued. Dow Chemical has recently patented a composition in which 2-oxazolene was added to an ethylene copolymer to produce a detectable increase in

bond strength.<sup>3</sup> Both National Starch<sup>4</sup> and Chemplex<sup>5</sup> have patented ethylene copolymer combinations with polypropylene to form improved hot melt adhesives.

Robots are perhaps one of the most significant developments which will profoundly affect the growth of hot melt adhesives. Robots are being evaluated in many industries, and their utilization is essentially assured. Fortunately, hot melt adhesives are easily adaptable to application by robots. Application is reliable and accurate and will lead to increased productivity and quality. The evidence suggests that if the partnership of robot and hot melt adhesives is understood and wisely applied, there will be a significant place for hot melt adhesives in the future.

The use of robotics in the auto industry appears to be a natural, but other areas may also exist. Penetration of the housing industry has been a goal of adhesive industry for sometime, so far largely unattained. But the slow shift to factory built modular homes may provide the opportunity for adhesive utilization.

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# Polyvinyl Acetal Adhesives

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Polyvinyl acetal resins are known for their excellent adhesion to a variety of surfaces. While the principal applications are adhesives for glass and metal, polyvinyl acetals provide structural adhesion for paper, fiber and plastics. They contribute flexibility and toughness to coatings. Excellent pigment binding capability has led to their use in printing inks, electrographic toners, and magnetic tape. The polyvinyl acetal polyvinyl butyral is almost exclusively used in the manufacture of laminated safety glass where optical clarity along with structural and adhesive performance is required.

Polyvinyl acetals celebrate 50 years of commercial production. Monsanto, DuPont, and Union Carbide have been the United States suppliers of polyvinyl butyral over its first half century of production. DuPont exclusively supplies safety glass interlayer under the trade name Butacite®. Union Carbide offers polyvinyl butyral resin as Bakelite®. Monsanto produces safety glass interlayer, Saflex®; polyvinyl butyral resin, Butvar®; and polyvinyl formal resin, Formvar®. Monsanto is the world's leading manufacturer of polyvinyl acetals.

This chapter introduces polyvinyl acetals through their application chemistry. Physical properties are tabulated or quantified. Various applications are summarized. The chapter closes with comments on the generally perceived structure of the polymer which through ad-

vancing analytical techniques has changed dramatically in recent years.

## CHEMISTRY

Acetals are formed by well known reaction of one molecule of aldehyde and two molecules of alcohol, as illustrated in Fig. 1.

Polyvinyl acetals are manufactured by reacting aldehydes with polyvinyl alcohol in the presence of an acid catalyst. Polyvinyl alcohols are manufactured by transesterification of polyvinyl acetate. The catalyst is either acid or base depending on the process. Polyvinyl acetate is polymerized from vinyl acetate by mass suspension or batch solution or continuous solution polymerization.

The acetals are terpolymers reflecting the three reactions which are used in their manufacture. The moieties are represented in Fig. 2. Manufacturers offer a variety of hydroxyl levels and molecular weight. The acetate level for commercial polyvinyl butyrals is usually low; offering little performance leverage for most applications. Higher acetate levels are common for the polyvinyl formals to improve solubility at the expense of strength and dimensional stability.<sup>1</sup>

Films of polyvinyl acetals are characterized by their high resistance to aliphatic hydrocarbons, mineral, animal, and vegetable oils; exceptions are castor and blown oils. They



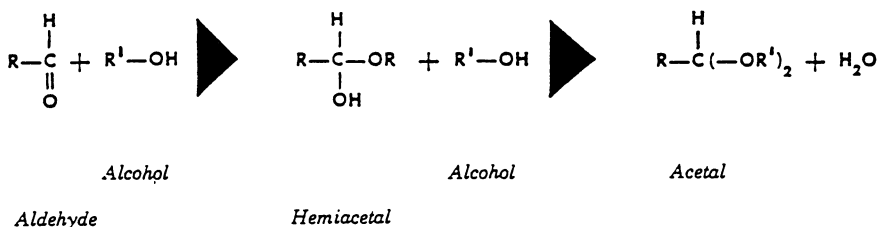


Fig. 1.

withstand strong alkalis but are subject to attack by acids. These properties are greatly enhanced when polyvinyl acetals are components in cured adhesives and coatings.

Many applications for polyvinyl acetal resins involve curing with a thermosetting resin to obtain a balance of properties. Generally, any chemical reagent or resinous material which reacts with secondary alcohols will react with acetals. Examples of probable chemistry for crosslinking polyvinyl acetals are shown in Figs. 3-7.

Hydroxyl level is the prime leverage on performance in most applications. The convention herein is to express hydroxyl level as weight percent.

The distribution of hydroxyl along the polymer chain is considered nominally random. However, as discussed in the section on basic research, recent work shows the polymer quite nonrandom. The distribution of hydroxyl can influence performance; particularly solution properties.<sup>2-4</sup> Matsuda's work<sup>4</sup> highlights the influence of the acetal process on the polyvinyl butyral heterogeneity. While commercial products are far less dramatically dissimilar than Matsuda's examples, it is recommended to

work with the manufacturer on performance optimization.

As with most polymers, molecular structure also leverages application performance. While this is beyond the scope of this chapter, C.A. Finch<sup>5</sup> is an informative resource.

### HEALTH, TOXICOLOGY, AND SAFETY<sup>6</sup>

No significant adverse health effects have been reported for Butvar or Formvar. In acute toxicity studies with rats and rabbits, polyvinyl butyral resin is practically nontoxic by oral ingestion ( $\text{LD}_{50} > 10,000$  mg/kg) or dermal application ( $\text{LD}_{50} > 7,940$  mg/kg). Butvar had only slight rabbit eye irritation (2.80 on a scale of 0-110) and did not irritate the skin. These resins are not considered carcinogenic.

Butvar and Formvar resin flash points are  $> 700^\circ\text{F}$ . The flammable limit for Butvar dust is 0.020 ounce per cubic foot in air. In application, Butvar and Formvar resins can be formulated to meet FDA extractability requirements. Butvar resins can be used in accordance with CFR regulations 175.105, 175.300, 176.170, and 176.180 as ingredients

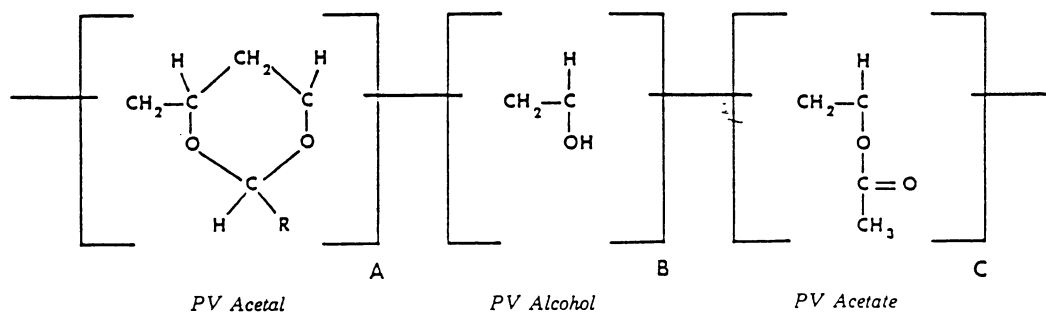


Fig. 2.

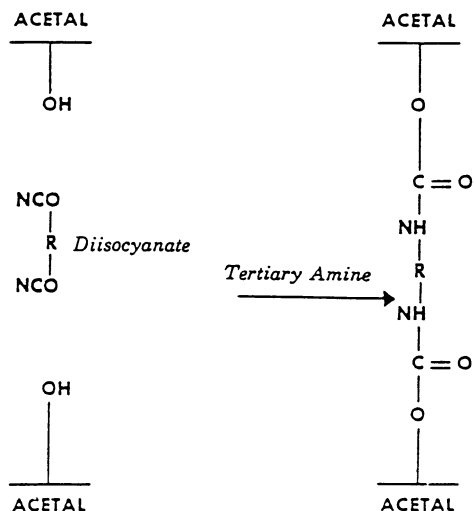


Fig. 3. Reaction with isocyanates.

of can enamels, adhesives, and components of paper and paperboard in contact with aqueous and fatty foods.

## PHYSICAL PROPERTIES

### Solubility

Polyvinyl butyrals are soluble in alcohols, glycol ethers, and selected mixtures of polar and

nonpolar solvents. Polyvinyl formals are soluble in mixtures of polar and nonpolar solvents. The higher acetate polyvinyl formal products are also soluble in glycol ethers, esters, and ketones. Table 1 is a representative list of applicable solvents. Examples of solubility parameters for commercial polyvinyl acetals appear in Table 2.

The influence of the terpolymer structure on solubility and compatibility can be generally described by Fig. 8.<sup>7</sup>

Aqueous dispersions of polyvinyl butyral are also available.<sup>8</sup> The dispersion particle size is  $< 1 \mu\text{m}$ . The dispersion is anionic and has a pH of 9–10.

### Compatibility

Polyvinyl acetal compatibility is principally driven by the hydroxyl or acetate content of the acetal. A general guide for compatibility of acetals with various solids is given by the examples in Table 3. Alloying with other solids is often used to alter the physical and chemical properties of acetals to achieve the best cost/performance ratio.

A wide variety of compatible plasticizers have been used. For many years, the univer-

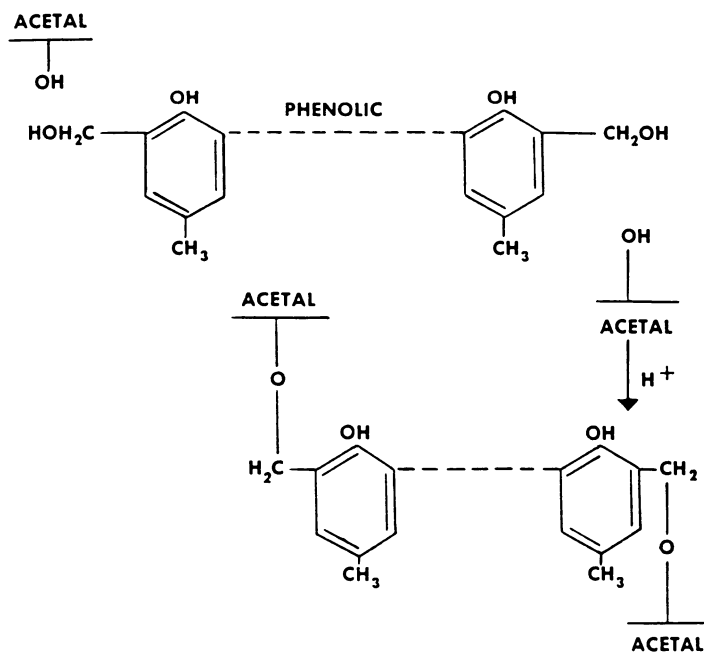


Fig. 4. Reaction with phenolics.

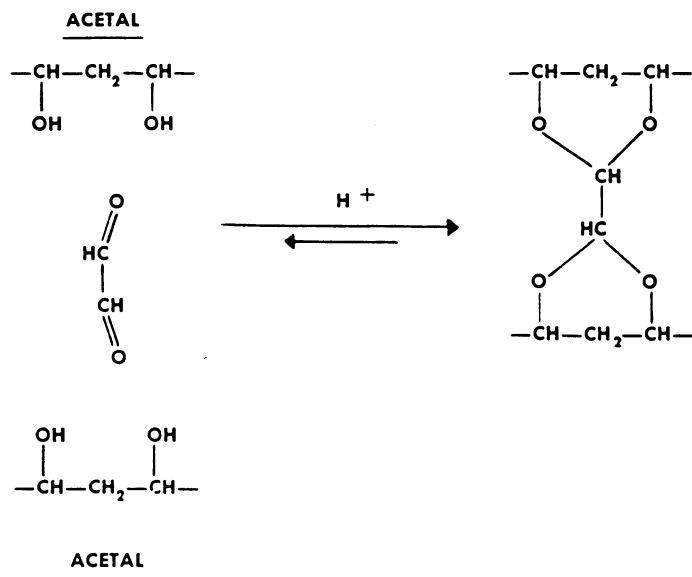


Fig. 5. Reaction with dialdehydes.

sally used plasticizer for polyvinyl butyral was triethylene glycol-*bis*(2-ethyl butyrate).<sup>9</sup> Recently this has been supplanted by adipates, tetraethylene glycol derivatives, butyl sebacate, ricinoleates, and others.<sup>10-18</sup> A list of compat-

ible plasticizers for the butyral can be found in Ref. 17. Recommended plasticizers for the butyral and formal can be found in Ref. 18.

Long-term compatibility of Saflex with various sealants can be found in Ref. 18. Sears

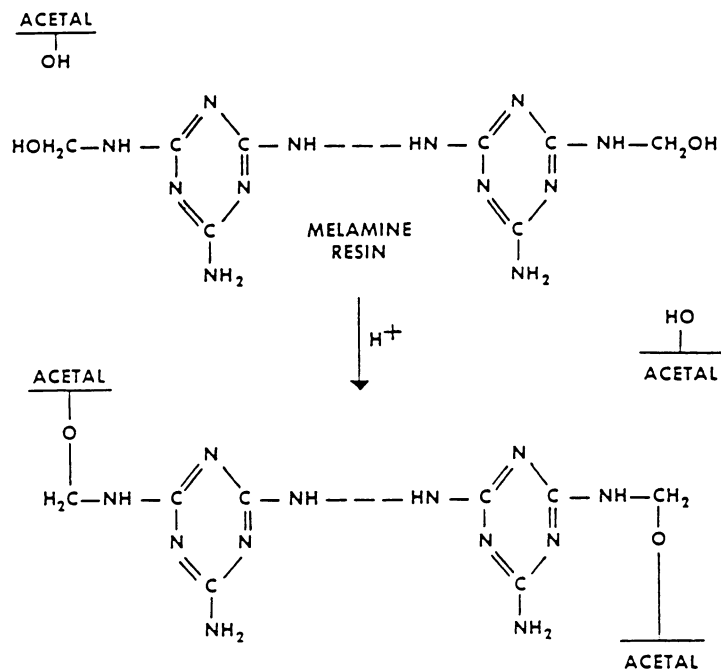
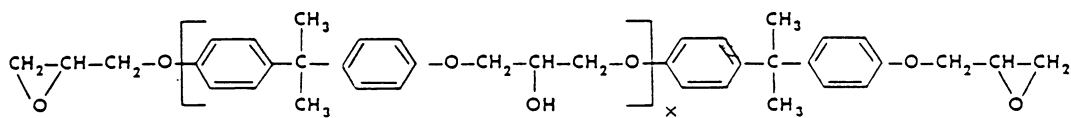


Fig. 6. Reaction with melamines.



Typical Epoxy Resin

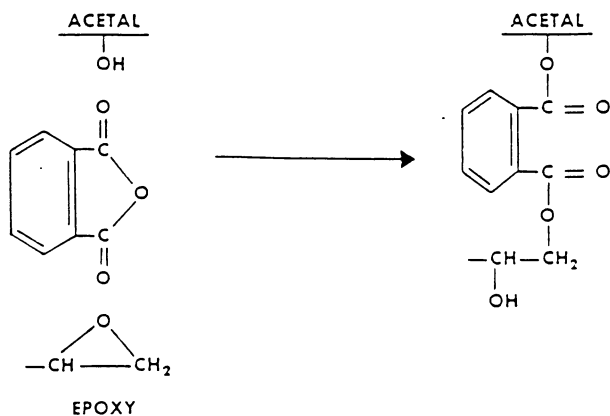


Fig. 7. Reaction with epoxies (anhydride cure).

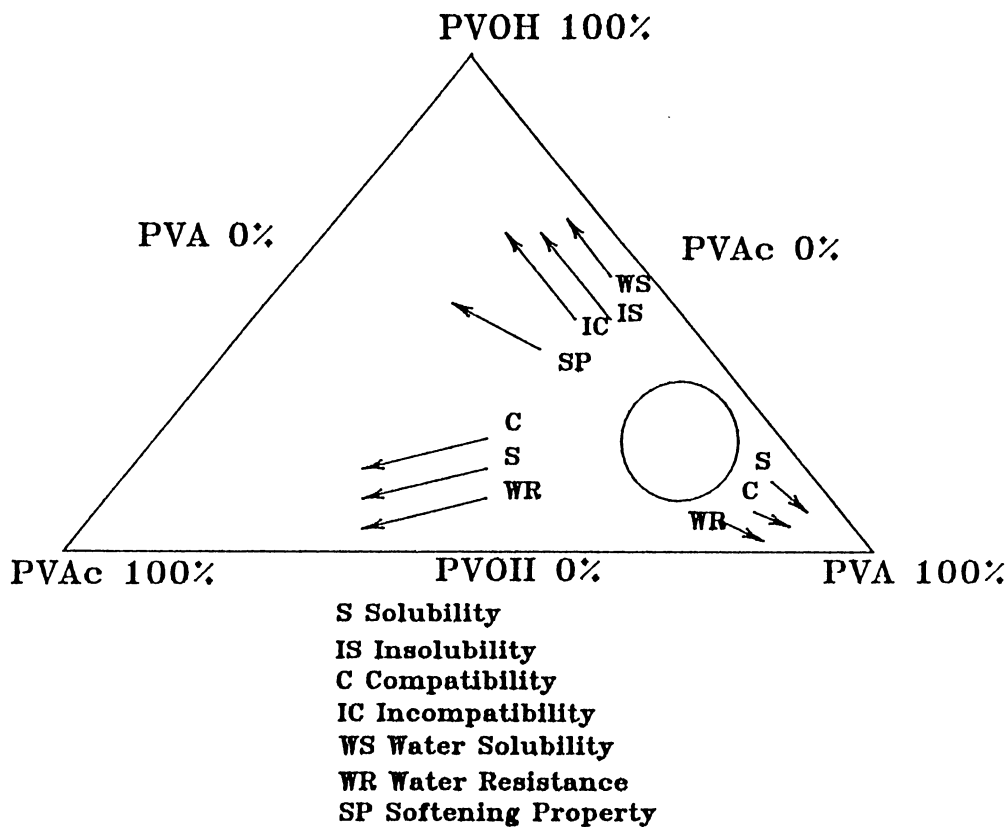


Fig. 8.

**Table 1. Solvents for Polyvinyl Acetal Resins.**

	<i>Polyvinyl Formal</i>		<i>Polyvinyl Butyral</i>	
	<i>Low Acetate</i>	<i>Medium Acetate</i>	<i>Low Hydroxyl</i>	<i>High Hydroxyl</i>
Acetic acid (glacial)	S	S	S	S
Acetone	I	I	S	I
<i>n</i> -Butanol	I	I	S	S
Butal acetate	I	I	S	I
Carbon tetrachloride	I	I	I	I
Cresylic acid	S	S	S	S
Cyclohexanone	I	S	S	S
Diacetone alcohol	I	S	S	S
Diisobutyl ketone	I	I	S	I
Dioxane	S	S	S	S
N,N-Dimethylacetamide	S	S	S	S
N,N-Dimethylformamide	S	S	S	S
Ethanol, 95 %	I	I	S	S
Ethyl acetate, 99 %	I	I	S	I
Ethyl acetate, 85 %	I	I	S	S
Ethyl "Cellosolve"	I	I	S	S
Ethylene chloride	S	S	S	S
Hexane	I	I	I	I
Isopropanol, 95 %	I	I	S	S
Methyl acetate	I	I	S	S
Methanol	I	I	I	S
Methyl "Cellosolve"	I	S	S	S
Methyl "Cellosolve" acetate	I	S	S	I
Methylbutynol	S	S	S	S
Methylpentynol	S	S	S	S
Methylethyl ketone	I	I	S	I
Methylisobutyl ketone	I	I	S	I
N-methyl-2-pyrrolidone	S	S	S	S
Nitropropane	I	S	I	I
Toluene	I	I	S	I
Toluene-ethyl alcohol (60:40 by weight)	S	S	S	S
Xylene	I	I	I	I
Xylene- <i>n</i> -butanol (60:40 by weight)	I	I	S	S

S = Completely soluble.

I = Insoluble or not completely soluble.

Source: Butvar/Formvar Technical Bulletin No. 6070A, Monsanto Chemical Co.

**Table 2. Solubility Parameter Ranges.**

	<i>Low Hydrogen Bonding Solvents</i>	<i>Medium Hydrogen Bonding Solvents</i>	<i>High Hydrogen Bonding Solvents</i>
Medium acetate polyvinyl formal	9.3-10.9	9.2-12.9	9.2-12.1
Low acetate polyvinyl formal	9.3-10.0	9.7-10.4	9.9-11.8
Low hydroxyl polyvinyl butyral	9.0-9.8	8.4-12.9	9.7-12.9
High hydroxyl polyvinyl butyral	Insoluble	9.9-12.9	9.7-14.3

Source: Butvar/Formvar Technical Bulletin No. 6070A, Monsanto Chemical Co.

**Table 3. Compatibility of Acetals.\***

	<i>Polyvinyl Butyral</i>		<i>Polyvinyl Formal</i>	
	<i>Low Hydroxyl</i>	<i>High Hydroxyl</i>	<i>High Acetate</i>	<i>Low Acetate</i>
Acrylate	I	I	I	I
Alkyd				
Rezyl 807-1	P	P	P	P
Duraplex C-49	P	P	P	P
Beckosol 1334-50EL	P	P	P	P
Alpha pinene				
Newport V-40	C	C	C	C
Cellulose				
Cellulose acetate	I	I	I	I
Cellulose acetate butyrate	P	P	P	P
Ethyl cellulose	P	P	I	I
Nitrocellulose, RS	C	C	P	I
Nitrocellulose, SS	C	C	I	I
Chlorinated rubber	I	I	I	I
Coumarone-indene	I	I	P	P
Epoxy				
Epi-Rez 540	C	C	C	C
Epon 1001, 1007	C	C	C	C
Araldite 6097	C	C	C	C
Fossil				
Damar	C	C	I	I
Isocyanate				
Mondur S	C	C	C	C
Ketone formaldehyde				
Advaresin KF	C	C	P	P
Melamine formaldehyde				
Resimene® 881 and 882	P	P	P	P
Resimene 730 and 740	P	P	P	P
Phenolic, unmodified				
Amberol ST-137	C	C	—	—
BKR-2620	C	C	P	P
BV-1600	C	C	—	—
BV-2710	P	P	C	C
GE75-108	C	C	C	C
Resinox® P-97	C	C	C	C
Rosin derivatives				
Pentalyn H	P	P	—	—
Staybelite Ester 10	C	P	—	—
Vinsol	C	C	C	C
Shellac	C	C	I	I

(Continued on page 430)

Table 3. (Continued)

	Polyvinyl Butyral		Polyvinyl Formal	
	Low Hydroxyl	High Hydroxyl	High Acetate	Low Acetate
Silicone				
SR 82	C	C	P	P
SR 111	C	P	P	P
DC 840	C	P	P	P
DCZ 6018	C	P	P	P
Sulfonamid				
Santolite® MHP	P	P	—	—
Urea formaldehyde				
Uformite F-240	P	P	P	P
Vinyl chloride copolymer	P	I	I	I
VAGH				

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C = Compatible in all proportions.

P = Partially compatible.

I = Incompatible.

\*Refers to film compatibility provided mutual solvents are used.

describes the approximate solubility and compatibility limits for polyvinyl butyral as quantified by solubility parameter, dielectric constant, and hydrogen bonding index in references.<sup>17,19</sup> This information is helpful in predicting the effectiveness of current environmentally acceptable solvents and plasticizers.

### Viscosity

Solution viscosity continues to be the measurement of choice for screening molecular weight of polyvinyl acetals. Where application performance requires fine control of molecular weight, solution viscosity is impaired by the complex solution behavior of these hydrophylic/hydrophobic polymers. Table 4 is an example of the relative sensitivity of solution viscosity of polyvinyl butyral in methanol to various parameters.

Finch<sup>5</sup> describes the difficulties in measuring solution viscosity of water soluble polymers. Since polyvinyl acetals have both water soluble and non-water soluble segments, solvent type plus inter- and intramolecular heterogeneity also influence viscosity.

Aggregation of the polymer in solution has

received considerable attention in developing gel permeation measurement of molecular weight.<sup>2,3,73</sup> For applications which require molecular weight to predict melt behavior, rheological measurement above 100°C avoids the distortion of aggregates. However, even melt viscosity is not a true measure of molecular weight and molecular weight distribution since branching and polymer nonlinearity influence high temperature rheology.

### Mechanical Properties

A wide range of strength and flexibility arise from the selection of aldehyde, polymer molecular length and the hydroxyl and acetate composition. Fig. 9 is extrapolated from the Monsanto product bulletin and compares three mechanical properties for a butyral and a formal of equal length, with acetates computed at 1.5 and 10 weight percent, respectively. The scales are in dynes/cm<sup>2</sup> divided by 10<sup>8</sup>. Fig. 9 illustrates the characteristically higher modulus of the formal. The circles amplify the scale. The average leverage for a change of 100 monomer units or 1 weight per cent hydroxyl is highlighted for three mechanical properties. For example, increasing the degree of poly-

**Table 4. Polyvinyl Butyral Solution Viscosity.**

		<div>←————— Average D.P. —————→</div>			
		1200	1700	1900	2100
Variable	$\Delta$ Var.	<div>←————— <math>\Delta</math>Visc. (cps) —————→</div>			
D.P.	100.0	17.1	32.5	—	48.0
MW/MN	0.5	7.0	18.7	—	34.1
OH	1.0	3.5	9.4	—	17.1
TS	0.1	—	—	17.3	—
Temp.	1.0	—	—	9.5	—

PVB Solution = 7.5 wt % — in methanol @ 20°C. Change in viscosity corresponding to change in:

D.P. = degree of polymerization, monomer units

MW/MN = polydispersity

OH = residual hydroxyl, wt %

TS = % solids in the PVB solution

Temp. = Solution temperature, °C.

merization (DP) of a butyral or formal 100 monomer units will increase the modulus of elasticity  $8 \times 10^7$  dynes/cm<sup>2</sup>.

Higher acetate will in general reduce modulus.

Mechanical hardness is dominantly a func-

tion of the aldehyde while hydroxyl and acetate have significant but less influence.

Polyvinyl acetals have excellent impact strength. The amount of energy absorbed by polyvinyl acetals is principally a function of the composite in which they are employed.

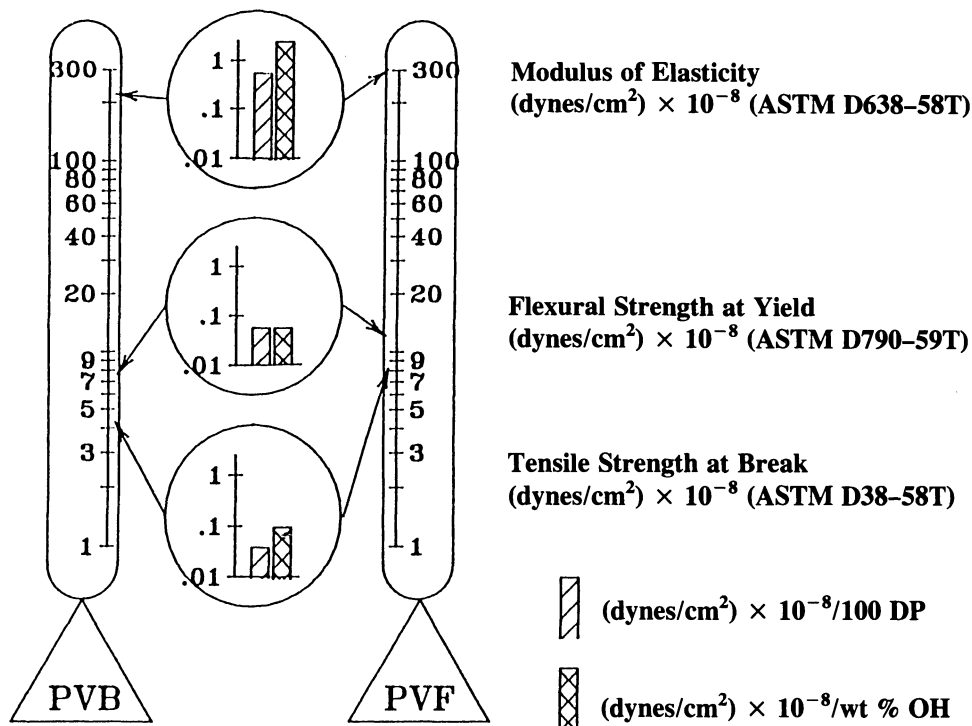


Fig. 9. Mechanical properties.



### Thermal Properties

As with mechanical properties, a wide range of thermal performance results from the selection of aldehyde, the molecular length and the hydroxyl and acetate composition. Fig. 10 compares three thermal properties for the equivalent butyral and formal computed in the mechanical property example. High temperature performance is dictated by the type of aldehyde and the polymer length. Polymer length has decreasing influence on thermal performance as the temperature decreases.

Predicting property performance of polyvinyl acetals at moderate temperature can be difficult. As is illustrated in Fig. 10, with the exception of acetal type, the moderate temperature thermal performance can be equally leveraged by the polymer length, and the level of hydroxyl and acetate. In addition, distribution of polymer composition and polymer length significantly influence applications.<sup>4,3,20</sup> A close working relationship with the manufac-

turer can be helpful for applications or preprocessing at moderate temperature.

The thermal glass transition temperature ( $T_{Gt}$ ) of polyvinylacetals of aliphatic aldehydes can be estimated from

$$T_{Gt} = 65 + 1.26 * (\text{OH} - 19.0) - 0.6 * (\text{OAC} - 1.5) + 46 * \ln(4/C)$$

OH and OAC are weight per cent hydroxyl and acetate.  $C$  is the number of carbons in the original aldehyde. The equation is centered for a typical polyvinyl butyral of 19 weight percent hydroxyl and 1.5 weight per cent acetate. For this typical butyral ( $C = 4$ ,  $\text{OH} = 19.0$ , and  $\text{OAC} = 1.5$ ) the equation reduces to a predicted thermal glass transition of 65°C. The standard error of the estimate is 3°C based on data from the general references and Ref. 21.

Polyvinyl acetals of any glass transition temperature between roughly 20°C to 120°C can be obtained by formulating with mixed alde-

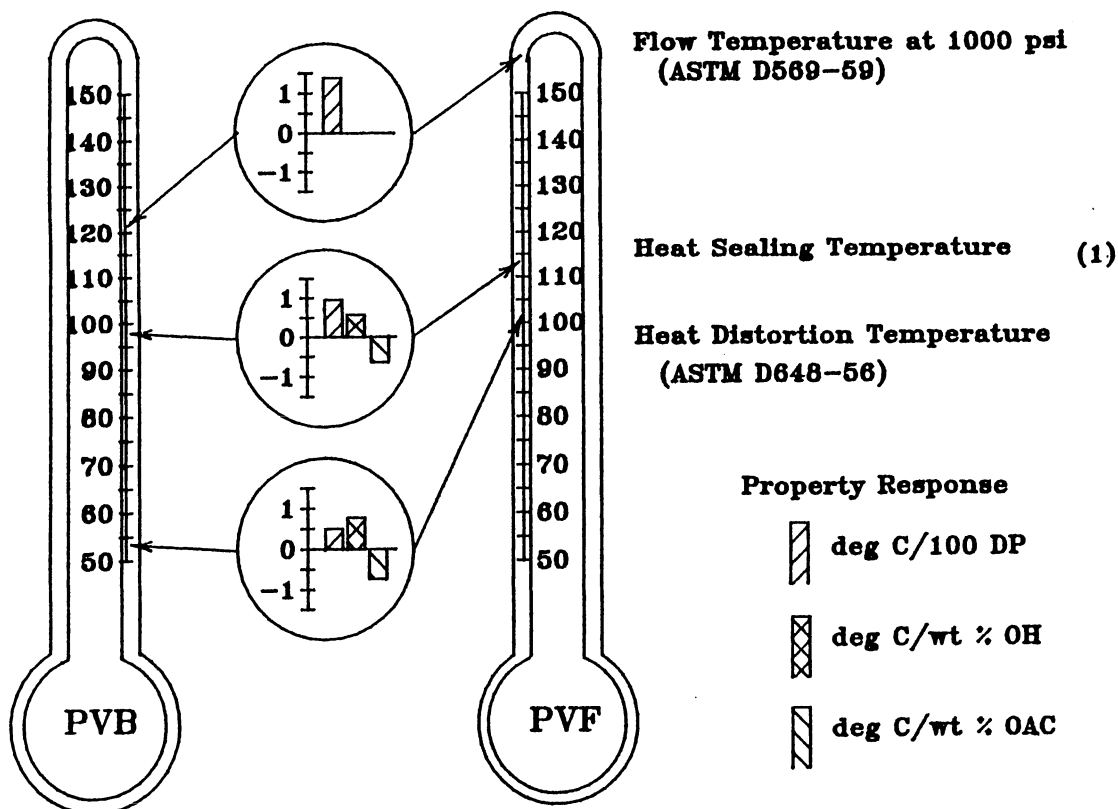


Fig. 10. Thermal properties.

hydes.<sup>21</sup> Glass temperatures for mixed aldehyde polymers can be estimated using the above equations by computing  $C$  on the basis of the aldehyde mole ratio used. For example: a polyvinyl acetal with a respective 30/70 mole ratio of butyral to hexyral would compute to have a  $C$  value of 5.4; at 19% hydroxyl the  $T_{Gm}$  equals 49°C.

For most applications the glass transition is far more practically manipulated with plasticizers. From Fitzhugh's data<sup>22</sup> the mechanical glass transition temperature lowers on average 1.3°C per part dibutylphthalate (DBP) added to one hundred parts polymer. The glass transition temperature for DBP plasticized polyvinyl acetals,  $T_{Gp}$ , can be estimated from the fraction of plasticizer  $P$  and the mechanical resin glass transition temperature  $T_{Gm}$ , using

$$\begin{aligned} \text{Ln}(T_{Gp}/T_{Gm}) \\ = -13.8 * P^{1.5} / (1 + 2.3 * P) \end{aligned}$$

Below the glass transition temperature the polyvinyl acetals of aldehydes with fewer carbons than butyral exhibit moduli above the  $2 \times 10^{10}$  dynes/cm<sup>2</sup> associated with fully amorphous polymers. The butyral and higher aldehydic carbon acetals are probably less oriented and exhibit moduli in line with fully amorphous polymers. The embrittlement temperature is precipitously lower for acetals with four or more carbons in the original aldehyde.

The butyral has commercially evolved as the dominant polyvinyl acetal; the butyral provides flexible toughness over a wide range of temperatures and at lower cost than the higher aldehydic carbon acetals. Where stiffer performance at higher temperatures is required, the formal provides significant property advancement at lowest cost.

## USES AS AN ADHESIVE

### Hot Melts

Polyvinyl butyral is an excellent base for hot-melt adhesives, particularly in applications with difficult-to-bond surfaces. The butyral resin is usually formulated with plasticizers, waxes, and other resins.<sup>23,24</sup>

### Thermosetting Adhesives.

Polyvinyl acetals are combined with other components to provide toughness, flexibility, and high adhesive strength in high performance thermosetting adhesives. Their use with olefins is described in references.<sup>25,26</sup>

### Adhesion to Metal

The first and most extensive use of polyvinyl formal is an insulator for electrical wire. A 1943 General Electric patent<sup>27</sup> describes the typical 105°C formulation. Polyvinyl formal resins have since been formulated into many different wire enamel applications. These include solderable enamels, high cut-through enamels, Freon-resistant enamels for hermetically sealed motors, and multicoat magnetic wires for 155–180°C performance.<sup>28–30</sup> Work to improve wire enamels is contained in Refs. 31–35.

Drum and can linings contain polyvinyl acetals. In addition to adhesion, the acetals provide coating uniformity, flexibility, toughness, and reduce cratering. They can be compounded and formed into baked coatings that have good chemical resistance and withstand postforming. The coatings can be formulated to meet FDA requirements.

A well known metal adhesion application is in washed primers. Application information is available.<sup>36</sup> Additional information is provided in the general references and Refs. 37 and 38. The Navy has long recognized the need to pretreat a metal surface prior to painting to inhibit corrosion and promote adhesion and specifies wash primers in MIL-P-15328C and MIL-C-8514B.

### Adhesion to Natural Surfaces

Polyvinyl butyral is the acetal usually selected for adhesion to natural surfaces. Application to wood<sup>39–42</sup> confers good holdout, intercoat adhesion, moisture resistance, flexibility, toughness, impact resistance, and protection against discoloration. Application to textiles, natural and synthetic,<sup>43</sup> improves stain and water resistance without noticeably affecting feel, drape, or color. Textiles with improved fire resistance, dyeability, or leatherlike char-

acteristics have been patented in the USSR and Japan.<sup>44-47</sup> Aqueous butyral dispersions are adhered to textiles where room temperature drying is important.<sup>8</sup> Polyvinyl acetals are selected as adhesives on paper in a variety of reproduction technologies: reprographics, photography, xerographic toners, and dielectric coatings.

### Green Strength Binder

Polyvinyl butyral adheres prefired molded parts in a variety of applications. These range from sand castings<sup>48</sup> for steel forging to interim tapes for high quality ceramics for electronics.<sup>49-53</sup> In addition to adhesion to the variety of inorganic components in these applications, polyvinyl butyral provides flexibility and strength to the unfired part. In some processes these parts have sufficient green strength to be machined.

### Composites

Polyvinyl butyral finds an important role in strengthening high strength plastics. DuPont's aromatic polyamide, Kevlar®, combined with polyvinyl butyral and phenol-formaldehyde, laminates into light-weight bullet-resistant helmets and armor plate.<sup>54-55</sup> Monsanto's Safflex SX laminates with polycarbonate to provide a transparent bullet-resistant glazing. DuPont offers an anti-lacerative sheeting which is a laminate of polyvinyl butyral and oriented polyethylene terephthalate and when adhered to glass provides protection against glass splintering on impact.<sup>56</sup>

### Adhesion to Glass

Perhaps the accolade which best suits the nearly half-century-old product of glass/plasticized polyvinyl butyral/glass is from John St. Clair.<sup>57</sup> In his article on the manufacture of laminated glass, Mr. St. Clair comments that he is not aware of any laminated glass made with polyvinyl butyral which could have been said to have failed through old age. A history of the product is available in Refs. 58-61.

In addition to longevity the product meets very stringent quality standards for consistent impact performance and optical quality. The principal use is automotive windshields. In re-

cent years architectural applications have been developed in which safety, security, sound control, and solar energy control are manifested.<sup>62,63</sup> The product permits freedom in design, and the market for architectural bent glass is growing.<sup>64</sup>

### Other Uses

The preceding examples of applications, while not comprehensive, illustrate the flexibility of polyvinyl acetals in application as well as function. Not discussed are applications in inks, dyes, printing plates, films, foams, filters, membranes, and sponges. Miscellaneous applications include combustible cartridges, wound dressing, surgical sutures, polarized lenses, fluxes for welding and soldering, and phonograph-record cleaners.<sup>65-72</sup>

### BASIC RESEARCH

Advances in analytical methods are gradually permitting quantification of structural heterogeneity independent from inter- and intramolecular compositional heterogeneity. This separation has been a long standing problem in determining accurate molecular weight data. Data by L. Mrkvickova<sup>2</sup> and P. M. Cotts<sup>3</sup> are consistent with unpublished work of E. E. Remsen.<sup>73</sup> NMR has also been helpful,<sup>74</sup> and two-dimensional NMR measurements have been made.<sup>75,76</sup> In spite of dramatic advances, quantification of structure and compositional heterogeneity sufficient to comprehensively predict application performance is well in the future.

### ACKNOWLEDGMENT

We wish to acknowledge our co-workers within Monsanto's Safflex and Resins business unit. We specifically acknowledge Drs. E. Lavin and J. A. Snelgrove for their earlier labors in this regard, and the preparation assistance of L. M. Daudelin and N. E. Franco.

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# Acrylic Adhesives

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In 1901, at Tuebingen, Germany, a doctoral candidate named Otto Rohm published a thesis describing liquid condensation products obtained from the action of sodium alkyoxides on methyl and ethyl acrylate. He also discussed the chemical nature of the polymer materials formed simultaneously in these reactions. With this work, Dr. Rohm put in motion a chapter of chemical history which blossomed in the ensuing half century into a significant commercial factor in the adhesives, plastics, coatings, and other industries. During this half century, a number of processes have reached commercial utilization for the manufacture of the acrylate monomers and for the variety of polymer materials which are derived from those monomers.

Polymeric products used in the design of solvent and waterborne acrylic adhesives as well as 100% solids reactive adhesives all have a number of characteristics in common. The most noteworthy of these features are:

- Low Temperature performance
- Broad adhesion spectrum
- Water resistance
- Easily formulated
- Excellent optical properties
- Durability
- Low toxicity

Acrylic adhesive polymers, both in aqueous emulsion form and solvent solution form, are

widely used as the basis for adhesives for pressure sensitive tapes, labels, and other decorative and functional pressure sensitive products. These applications capitalize on the versatile adhesion and the excellent aging characteristics of this class of polymer.

Acrylic materials are also widely used as elastomers and thickener components in a variety of waterborne construction adhesives, laminating adhesives, and packaging adhesives. Sometimes, the polyacrylate portion of these adhesives is minor, contributing a thickening function to such other elastomers as styrene-butadiene latex and polyvinyl acetate compounds. A variety of specialty laminating adhesives, in both filled and unfilled form, utilize acrylic elastomers to bond dissimilar surfaces in operations which are performed via wet laminating, pressure sensitive laminating, contact bonding, and heat sealing operations.

Finally, acrylic chemistry is the basis for a number of 100% solids reactive engineering adhesives used in structural bonding applications, generally involving metal or plastic non-porous surfaces.

## TECHNOLOGY

### Chemistry

Acrylic adhesive polymers are synthesized from a wide selection of acrylic and methacrylic es-

ter monomers and almost always with low levels of monomers having pendant functional groups (for post crosslinking and/or special adhesion needs). More specifically, acrylic adhesives are based mainly on ethyl, butyl and 2-ethyl hexyl acrylate monomers, plus small quantities of methyl methacrylate, and acrylic and/or methacrylic acids, and other specialty acrylic monomers. Frequently, the acrylic monomers are copolymerized with other vinyl monomers such as vinyl acetate, vinyl chloride, styrene, etc. The high reactivity of vinyl groups permits the synthesis of linear polymers of very high molecular weight.

Most commercial processes are free-radical-type addition reactions conducted at elevated temperature in the presence of an initiator. Acrylic adhesives are made in a variety of physical forms, such as organic solutions, aqueous emulsions, suspensions, and carrier-free solid materials that are melt applied. Acrylics are available as thermoplastics, which melt and flow at high temperatures, and as semireactive or thermosetting crosslinkable systems which yield solvent- and heat-resistant polymers. In contrast, water soluble polymers can be made through proper monomer selection and functional group cappings. Chemically, these products are long chain polymers of methacrylate and acrylate esters. The physical properties of the acrylic polymers are influenced by the alpha position entity of the acid (hydrogen atom or methyl group) and by the length of the alcohol side chain modification.<sup>1</sup> See Fig. 1.

The acrylate polymers have an alpha hydrogen adjacent to the carbonyl group and, therefore, have more rotational freedom than the methacrylates. The substitution of a methyl group for the hydrogen atom (producing a methacrylate polymer) restricts the freedom of rotation of the polymer (steric hindrance) and thus produces harder, higher tensile strength and lower elongation polymers than their acrylate counterparts.

The ester side chain group also affects properties significantly. As the ester side chain becomes larger, the tensile strength of the polymer is decreased and its elongation increases.

Various monomers impart characteristic film properties to the acrylic polymer (see Table 1). These monomer modifications also affect polymer polarity and solubility, as well as the glass transition temperature of the polymer.

The characteristic properties of a polymer are greatly influenced by the conditions of polymerization. Variations in catalyst level, reaction time, temperature, and monomer concentration make it possible to adjust the polymer's molecular weight and ultimately its physical properties.

Solution thermoplastic acrylics form coherent films simply by solvent evaporation without post-filming reactions taking place. Therefore, the properties of thermoplastic resins depend primarily on the necessity of physical entanglements between long chain molecules and secondary bonding forces (<5 kcal/mole). Thus, it is possible to obtain with the same monomer

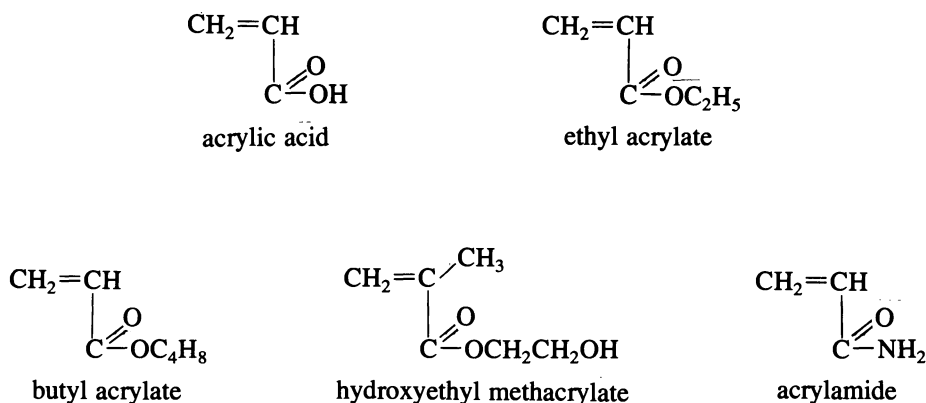


Fig. 1. Chemical structures of adhesives.

**Table 1. Mechanical Properties.<sup>2</sup>**

	<i>Tensile Strength (psi)</i>	<i>Elongation (%)</i>
<b>Polymethacrylate</b>		
Methyl	9,000	4
Ethyl	5,000	7
Butyl	1,000	230
<b>Polyacrylates</b>		
Methyl	1,000	750
Ethyl	33	1,800
Butyl	3	2,000

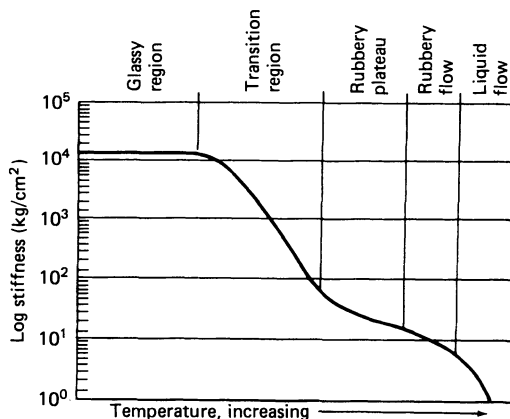
esters, by molecular weight variation, polymers with broad variation in viscoelastic mechanical properties.

The viscosity of solution polymers increases directly with molecular weight. Performance properties begin to plateau as molecular weight increases, but viscosity continues to increase. Thermosetting solution acrylic resins are polymerized to lower molecular weight than thermoplastic acrylics, since they attain their property performance by conversion to infinite three-dimensional networks by chemical reaction (forming primary chemical bonds).

### Glass Transition Temperature ( $T_g$ )

The glass transition temperature of acrylic polymers is one of the most important characteristics governing many of the properties that are important in adhesives.

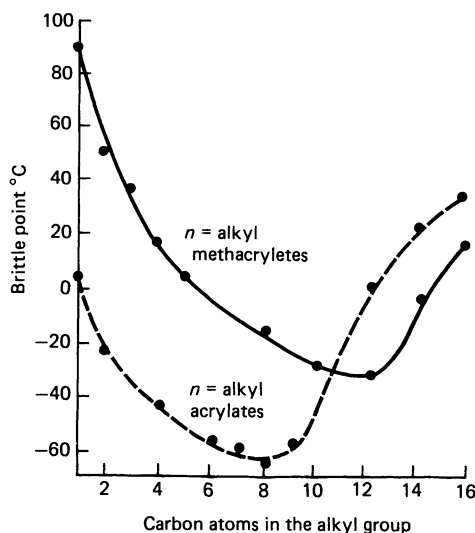
All polymers exhibit a second order transition temperature range at which the polymer changes from a hard, glasslike solid to a rubbery or liquid state, depending on the molecular weight and/or chemical bonding. This transition is a reflection of the entropy (freedom of motion) characteristics of the polymer. At a certain temperature range, polymer molecules receive sufficient thermal energy to break out of their "frozen" configurations into a state of rapid segmental motion. In this highly agitated state, the physical entanglements between the long-chain molecules have more freedom of motion and thus impart the rubbery or tacky semi-solid properties (see Fig. 2). As shown by Rehberg and Fisher,<sup>4</sup> the brittle point of the homopolymer drops to its lowest value with 8 and 12 carbon atoms in the alkyl group and there-

**Fig. 2.**

after increases with increasing chain length of the alcohols, the polymers attaining a wax-like consistency (Fig. 3).<sup>3</sup>

Numerous investigations have been made into the factors influencing  $T_g$ . Most of these are related to the effect of molecular structure and chemical composition:

1. Side Chain Effects. The further apart the chains in the polymer, the greater the segmental mobility.
2. Chain Stiffness. The extra  $\text{CH}_3$  group in a methacrylate causes additional steric hindrance to movement which, in turn, raises the glass temperature.

**Fig. 3.** Brittle points of polymeric *n*-alkyl acrylates and methacrylates.<sup>4</sup>



3. Branching. A branched group on the side chain also raises the  $T_g$ ; *t*-butyl has a much higher  $T_g$  than *n*-butyl. These trends are illustrated in Table 2.
4. Copolymers, Internal Plasticization. By copolymerizing more than one type of acrylic monomer, polymers with intermediate  $T_g$  values can be prepared. Fox<sup>5</sup> has proposed the following equation for calculating the  $T_g$  of copolymer from known values of the homopolymers:

$$\frac{1}{T_g} (\text{copolymer}) = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} + \frac{W_n}{T_{gn}}$$

5. Crosslinking. Crosslinking prevents the onset of rubbery flow by the formation of chemical bonds which impede segmental motion.

### Crosslinked Thermosets

Thermosetting acrylic resins are characterized as vinyl addition polymers having pendant chemical groups capable of further reaction. The most important commercial materials used at present contain amide, carboxyl, hydroxyl, or epoxy functionality. As in other interpolymer systems, the film properties may be altered in several ways: variation in backbone composition, use of curing catalyst, and variation in the amount of crosslinking agent.

Catalysts, either internal or external, have the effect of accelerating cure response at a lower bake temperature. Curing temperatures are normally reduced by 50–100°F by the addition of catalyst.

The level of crosslinking agent added should be determined for the various thermosetting types to determine optimization of property

performance. If the degree of crosslinking is too high, brittle products are produced and, conversely, too low a level results in poor resistance properties. Table 3 outlines the typical catalysts and crosslinkers for the thermosetting acrylic systems.<sup>6</sup>

### BONDING PROCESSES

We can classify acrylic adhesive bond formation into four different processes:

- Pressure sensitive bonding
- Wet laminating
- Contact bonding
- Heat and pressure bonding

These approaches are dictated by coating and drying requirements, substrate porosity, water and solvent sensitivity, open time requirements, and urgency of bond strength development. Acrylic polymers are being used in all the above bonding processes. A comprehensive review of each follows.

#### Pressure Sensitive

Pressure sensitive adhesives form a permanent tacky film after the evaporation of the liquid phase or after cooling of a hot melt. Bonding is effected by slightly pressing the adhesive surface onto the adherend. Pressure sensitives can demonstrate a wide range of adhesive properties, from permanent bondings to removable tapes and films.

A number of polymeric raw materials are used in the pressure sensitive adhesive market. They include: natural rubber, polyisobutylene, polyvinyl ether, various types of synthetic rubber such as styrene-butadiene and -ethylene copolymers, polyurethane, and acrylics.

The most important properties of any pressure sensitive adhesive are a balanced relationship of tack, cohesion, and adhesion. To these properties, acrylic pressure sensitives add the valuable qualities of heat resistance and resistance to aging and UV radiation. Another desirable characteristic of acrylics is that, in general, tackifiers are not required because tack can be designed into the polymer through the proper choice of acrylic monomers. These and other properties of acrylic pressure sensitive

**Table 2. Glass Transition Temperature,  $T_g$  (°C).**

<i>Ester</i>	<i>Methacrylate</i>	<i>Acrylate</i>
Methyl	105	9
Ethyl	65	–22
<i>t</i> -Butyl	107	41
<i>s</i> -Butyl	48	–43
<i>n</i> -Butyl	20	–54
2-Ethylhexyl	–10	–82

**Table 3. Catalysts and Crosslinkers for Thermosetting Acrylic Systems.**

<i>Pendant Group on Acrylic or Methacrylic Polymer</i>	<i>Reactive Monomer Containing Pendant Group</i>	<i>Resin Co-reacted to Effect Cure</i>	<i>Catalyst</i>
— CONHCH <sub>2</sub> OR	Acrylamide or methacrylamide converted with CH <sub>2</sub> O + alcohol to an ether	Epoxy, alkoxy aminoplasts, carboxyl containing	Acidic—AA or MAA (internal); H <sub>3</sub> PO <sub>4</sub> , PTSA
— COOH	Acrylic or methacrylic acid	Epoxy	Basic—benzyl, dimethylamine, triethanolamine
— CH <sub>2</sub> OH	Hydroxyethyl or hydroxypropyl methacrylate	Alkoxy aminoplasts	Acids
$\begin{array}{c} \text{—CH—CH—} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$	Glycidyl methacrylate	Carboxylic polymers	Acidic—MAA or AA (internal), NH <sub>4</sub> Cl, PTSA; Basic—DMAEMA (internal) quat-ammonium compounds

AA: acrylic acid. MAA: methacrylic acid. PTSA: *p*-toluenesulfonic acid. DMAEMA: dimethylaminoethyl methacrylate.

adhesives have gained them a significant share of the pressure sensitive market.

Principal applications for pressure sensitive acrylics are a broad assortment of tapes and labels, decals, and other decorative films. Acrylics also have some uses in laminating adhesives, primarily for film-to-film laminates. In addition, acrylics have been used in sound-deadening pads for automobiles and appliances.

To be suitable as a pressure sensitive adhesive, acrylic adhesives are based on acrylic esters with four or more carbon atoms, the most common of which are *n*-butyl acrylate and 2-ethylhexyl acrylate. These acrylates are copolymerized with other monomers such as acrylonitrile, methyl methacrylate, other acrylates, styrene, vinyl acetate, and  $\alpha,\beta$ -unsaturated carboxylic acids, depending on the adhesive properties required.<sup>7</sup> This versatility inherent in the acrylics has led to the design of products requiring widely different adhesive properties, from those of permanent labels and high performance tapes to removable labels and films.<sup>8</sup>

Pressure sensitive acrylic adhesives are available in the form of solutions in organic solvents, aqueous emulsions, and 100% solid (hot melt). Traditionally, acrylic adhesives have been provided in organic solvents, but re-

cently aqueous emulsion acrylic polymers have been developed that in many cases match the performance of the solvent based acrylic adhesives.<sup>8</sup> The ability to coat water-based systems on high speed film coating machines, along with the obvious advantages in lower cost, safety, and environmental protection, has led to a rapid growth in the use of water-based adhesives. While the acrylic hot melts have offered the same advantages, there have been technical difficulties in obtaining adequate cohesive strength without an excessively high melt viscosity which have limited their commercial use.

**Formulation.** Unlike the natural rubber pressure sensitive adhesives, acrylic adhesives are often supplied in a ready-to-use form. Natural rubber adhesives require time-consuming and costly mastication of the rubber followed by dissolving in solvent.<sup>9</sup> In addition, they must be formulated with a tackifier resin and antioxidants, neither of which is required with an acrylic adhesive. The acrylic adhesives are known for their good UV and oxidative stability while the rubber-based adhesives, because of their chemical unsaturation, are poor in these properties. In general, tackifiers are not required with acrylic adhesives as tack can be designed into the polymer by the proper choice of

acrylic monomers. However, if very high tack is required, some of the tackifiers used with natural rubbers, e.g., rosin ester and low molecular weight polyaromatics, can be added to the acrylic adhesive.<sup>10</sup>

Two critical parameters of an aqueous adhesive formulation are its viscosity and rheological properties.<sup>11</sup> Different types of conventional coating equipment will require different viscosities, and the rheological properties will determine the flow and leveling characteristics of the formulation.

In solution-based adhesives, the viscosity is controlled by the type of solvents used and the solids content of the adhesive. The rheology of solution acrylic adhesives is generally Newtonian. In aqueous emulsions, the viscosity of the unformulated adhesive is low—around 100 cps—and, if needed, a thickener is added to raise viscosity. Aqueous emulsion-based adhesives generally have non-Newtonian rheology; that is, they experience significant viscosity changes as a function of shear rate. Usually emulsions are thixotropic, i.e., shear thinning, but in rare cases a dilatant rheology can occur, i.e., an upward viscosity progression with increasing shear rate. A shear rate/viscosity profile should be obtained for all new aqueous adhesives.

Thickeners that are commonly used in acrylic emulsion adhesives include alkali-soluble acrylic emulsions, polyvinyl alcohols, and cellulose. By proper choice of thickener the rheology properties can be optimized for specific coating head configurations.

This flexibility has proven invaluable in the design of “coater-ready” aqueous adhesives which are specifically designed for a wide range of application techniques. These techniques include reverse roll coating, curtain coating, gravure coating, and spray application. Key characteristics built into the aqueous adhesives to permit such a wide variety of application techniques include:

- Good flow and leveling (rheology)
- Low foam generation
- Good substrate wet-out
- Mechanical stability
- Uniform, efficient drying

The aqueous-based adhesives may require the addition of a surfactant to help stabilize the dis-

persion against shear-induced coagulation and to achieve good wetting on low energy surfaces, such as a silicone release liner. However, the presence of excess surfactant can lead to excessive foam generation during coating, which can affect the coating properties. Excess foam can be controlled with a defoamer, but certain defoamers can cause poor wetting of the surface, as evidenced by fisheyes and cratering. Thus a careful balance between surfactant and defoamer is required to get a good coating.<sup>12</sup>

**Properties and Testing.** The adhesive requirements for a pressure sensitive adhesive will vary greatly with end use. While each application will have certain specific tests, the three most common adhesive tests are peel adhesion, shear (creep) resistance, and tack.<sup>13</sup> There are standard test procedures developed for these tests by PSTC,<sup>14</sup> ASTM,<sup>15</sup> and the Tag and Label Manufacturers Institute.<sup>14</sup>

*Peel adhesion*<sup>14,15</sup> is the force required to break the adhesive bond between two substrates. Usually this is measured by peeling back the adhesive backing at 180° or sometimes 90° from the surface at a standard rate and under carefully controlled environmental conditions. In some cases the bond is broken within the adhesive layer, not at the surface. This is called *cohesive failure*, and is generally acceptable for permanent applications but not for removable applications.

*Shear adhesion*<sup>14</sup> is the ability of a tape to resist the static forces applied in the same plane as the backing. It is a measure of the cohesive strength of an adhesive. Usually it is expressed in the time required for a given weight to cause a given area of adhesive to come loose from a vertical panel.

*Tack* is the measurement of the quick grab or stickiness of an adhesive. Tack is a surface phenomenon that is not always indicative of an adhesive's performance. There are several methods of measuring tack. One test is called the *quick stick*.<sup>14</sup> It is a measure of the force required to remove a tape at a 90° angle from a surface to which it has been applied under no other pressure than the weight of the tape itself. Another version of this test is called *loop tack*, in which the pressure sensitive tape is applied in a loop form using only the pressure of the

tape as the applied force. Another common test is the *tack rolling ball test*.<sup>14,15</sup> A steel ball is rolled down an inclined trough onto an adhesive. The length of adhesive required to stop the ball is measured and used to quantify the tack of an adhesive. The higher the number, the poorer the rolling ball tack. It should be noted that the correlation between quick stick (loop tack) and rolling ball tack is sometimes poor.<sup>15</sup> Formulations containing high concentrations of tackifiers can have excellent quick grab properties as measured by quick stick and loop tack, but high rolling ball tack. One other tack measurement is the Polyken Probe.<sup>15</sup> This is an instrument that measures tackiness by bringing the tips of a flat probe into contact with an adhesive under known conditions and then measuring the force necessary to break the bond. The force is measured in grams and reported as *grams of tack*.

### Contact Bonding

Contact adhesives are used where immediate and high bond strength is required. The adhesive is applied to both surfaces to be joined, and allowed to dry completely. Then the substrates are bonded, generally with hand pressure for consumer applications and nip rollers and presses for industrial bonding operations. Open time can vary from several minutes to several hours.

Contact adhesives are used to manufacture furniture and countertops of high pressure plastic and particle board, movable and permanent office partitions, assemblies of cold rolled steel to honeycomb cardboard, and foamed substrates for both steel doors and prefabricated curtain walls. Other applications for contact adhesives include small product assembly such as toys, sporting goods (with substrates such as leather), aluminum foil, plastic films, rigid plastic and foams.

Use of contact adhesives is a good solution for a variety of miscellaneous bonding problems in the home where nonporous surfaces are involved and immediate high bond strength is a requirement. The adhesive is applied via paint brush or paint roller, with normal application recommending two coats to be applied to the nonporous surface, chipboard in this case.

Aqueous acrylic contact adhesives contain no solvents which could represent inhalation or flammability hazards.<sup>16</sup> In addition to eliminating these hazards, some aqueous acrylics provide other benefits:

- Heat resistance
- Clarity
- Adhesion to a broad spectrum of substrates, including plastic and metals
- Ease of formulation
- Ease of handling—can be applied by brush, spray, or roller
- Ease of cleanup

While some of the earlier acrylics had a short open time (bonding window), the more recent entries permit the homeowner more flexibility in bonding time.<sup>17</sup> Thus, good bonding may be achieved for hours after the clear point is reached.

### Heat and Pressure Bonding

With heat-activated bonding techniques, a non-blocking (tack-free) film is applied to one substrate and later reactivated by the application of heat, which produces adhesive flow onto the second substrate during a nipping operation, thereby effecting a bond on cooling. Open time is very short, in the several-second range. It should be noted that, generally, acrylics may require longer dwell time than crystalline polymers since, as is typical of amorphous polymers, they do not show the sharp melting or freezing points characteristic of crystalline polymers. This bonding technique provides immediate bond strength, as do contact adhesive bonding and pressure sensitive adhesive bonding. Obviously, this method is not suitable for heat sensitive substrates. Some typical examples can be found in heat-seal food packaging and a variety of vacuum forming operations such as automotive door panels.

Applications where acrylics see use include the heat sealing of cellophane to metal foil and metallized polyester film or polypropylene film. These films are used primarily in the food packaging area. Other applications are in the overlay area, where clear or photoembossed vinyl films are bonded to wood substrates to produce a simulated expensive wood grain finish.

### Vacuum Bonding

Vacuum bonding is practiced in the manufacture of various automotive interior PVC trim items such as door panels, instrument panels, and van side panels. The process consists of spraying adhesive on the rigid fiberboard or plastic (usually an ABS substrate), drying the substrate, then inserting it into a vacuum forming unit where the preheated vinyl is mated to the rigid ABS or chipboard and maintained under vacuum and the residual heat for several seconds. Immediate high bond strength is required, since the vinyl in some cases has been elongated several hundred percent to conform to contoured areas.

The rigid substrate, usually containing contoured and deep-draw areas, is mounted to a mated metal mold which has predrilled holes to allow sufficient vacuum draw on the surface of the rigid fiberboard or plastic. Substrates like ABS that are vacuum barriers themselves also require holes to allow vacuum forming.

### Wet Laminating Adhesives

The wet laminating approach allows for immediate but relatively low strength bonding of two surfaces. A short open time dictates that the substrates be mated while the adhesive is still wet. In addition, at least one of the substrates must be porous to allow water or solvent to escape through the laminate. Drying occurs subsequent to substrate combination. Examples of the wet laminating technique include bonding of printed vinyl film to fabric for wallpaper and vinyl to foam for soft goods or furniture covering.

Waterborne adhesives, used almost exclusively in wet laminating operations, offer non-flammability and the low toxicity of acrylic-based products. These two characteristics are especially significant, since the volatile carrier migrates into the porous substrate and subsequently dissipates into the environment after bond formation has been completed.

Wet laminating allows for adhesive polymer selection from permanently tacky pressure-sensitive-type products in the  $T_g = -40^\circ\text{C}$  range to fairly stiff polymers that require some coalescence for adequate film formation. Generally, the lower  $T_g$  polymers are used to

manufacture flexible laminates, while the stiffer analogs find more use in the product assembly areas.

Typically, aqueous acrylic emulsion polymers of 5,000–10,000 cps viscosity are coated onto the plastic film using roll coat techniques set to yield coating weights of 15–35 pounds per ream. Within a few feet after the coating station the second substrate (i.e., cotton/polyester fabric, polyurethane foam, etc.) is married to the wet plastic and then nip bonded. The laminate may then pass through a series of heated rolls, lamp station, and finally cooling rolls prior to being wound onto the take-up roll. Line speeds are relatively slow, generally being in the 30–90 feet per minute range. Initial adhesion testing is usually a subjective hand peel test, with fabric or foam failure being the ideal target. More sophisticated tests may be done after the laminate has aged at least 24 hours. These may include standard T-peel tests on conventional testing machines. If water sensitivity is a criterion, the T-peels may be performed after an overnight water soak of the preconditioned laminate. (Preconditioning usually consists of a 3–7 day aging at 50% relative humidity and  $75^\circ\text{F}$ .)

Typical wet bonding applications involve bonding of films, paper, or plastic sheet to such nonporous surfaces as fiberglass, fabric, thin gauge open cell foams, and plywood or chipboard. The diversity in substrate surface energy, porosity, combining and drying techniques, and in-service end use performance requirements demands careful adhesive selection.

Bonding of vinyl film, paper, or foil to fiberglass for a variety of insulation products (e.g., acoustical tile, roll insulation, fiberglass/fiberglass for increased thickness, rigid fiberglass scrip/foil board fire retardant modified) is normally accomplished by overcoat or spray application of the adhesive to the paper, film, or foil.

Various gauge PVC and styrene films are bonded to a variety of fabrics and foams for miscellaneous soft goods applications such as luggage, sporting equipment, lamp shades, and wearing apparel. The bonding technique normally employs roller coat application with a gravure cylinder of the adhesive to the film, and

at times a partial dry before nipping to the fabric or foam. Wet tack or wet grab is an important criterion, since upon cooling there can be differential expansion of the two substrates. This can result in a variety of surface imperfections in the final product—especially when thin films are used.

Vinyl film, saturated paper, and fabric are bonded to plywood, chipboard, and steel to produce a variety of decorative panels, from simulated wood paneling to fabric-covered modular office sections. Generally, the adhesive is coated onto the rigid substrate via roll coater or spray application. Roll coater adhesive application to plywood and chipboard generally requires more than one pass for sufficient adhesive deposition, since the surfaces tend to absorb the adhesive. The primer or sealer coat is generally dried completely before a second coat is applied. Then, this second coat is subjected to a partial dry before nipping—sometimes under heat—to the decorative surface film. When the flexible laminate is bonded to a metal surface such as office partition sections, the adhesive usually is deposited via spray application onto the metal.

The wet bonding of rigid plastic sheet (high pressure plastic) to chipboard requires that the laminated sections be maintained in a rigid position until the adhesive has completely dried and crosslinking, if applicable, has commenced. The adhesive is roll coated or spray applied to the chipboard.

### Filled Adhesives

The broad spectrum of adhesion displayed by acrylic adhesives make filled acrylics excellent candidates for bonding substrates made of cellulose, leather, fabric, ceramic, foil, plastic, metal, and various foams. Typical examples include panel and subflooring adhesives, decorative brick mastics, ceramic tile adhesives, carpet adhesives, floor tile adhesives, and contact adhesives.

Acrylics permit high pigment loading. The outstanding pigment-binding capability, adhesion, and durability of acrylic polymers allow formulation at high pigment-to-binder ratios. This permits production of cost-efficient for-

mulations that still retain acrylic permanence properties.

With their wide range of high specific adhesion, acrylic emulsions may be used in a variety of formulations for different end uses. This permits the compounder to reduce inventory and storage costs.

Filled adhesives typically are designed for the construction and do-it-yourself trade. Filled adhesives consist primarily of the base polymer, fillers such as calcium carbonate or clay, solvents, surfactants, dispersants, preservatives, and thickeners. Formulations are specifically tailored for numerous end uses including brick mastics, carpet tile and continuous carpet adhesives, floor tile adhesives, ceramic tile, subflooring, and panel adhesives.

**Brick Mastics.** Brick mastics are the most highly filled adhesive formulations and are used to attach decorative brick and stone for both interior and exterior applications. The benefits of acrylic resins for brick mastics are specific adhesion, water resistance, weatherability, excellent flexibility retention, and formulating versatility.

The formulation provided in Table 4 is a starting point recommendation. Further adjustments to obtain desirable color texture and handling properties can be made.

**Carpet Tile Adhesive.** Carpet tiles and continuous carpeting can be adhered to the floor

**Table 4. Brick Mastic Adhesive—Moderately Extended.**

<i>Components</i>	<i>Parts by Weight</i>
Rhoplex AC-64 (60% solids)	100.0
Triton X-405	1.4
Tamol 850	0.7
Foamaster	0.4
Biocide	0.2
Propylene glycol	5.0
Varsol	2.0
Camel Carb	50.0
#60 Sand	25.0
#45 Sand	25.0
Sno Cal Clay	20.0
Cellufloc	6.0
Hi Sil 422	5.0
Acrysol ASE-60/Water (1/1)	1.5
Water	1.5

with a variety of adhesives products. These range from essentially nonfilled pressure sensitive adhesives modified to allow application by brush, paint roller, or notched towel, to very highly filled adhesives similar to those used for applying vinyl and vinyl asbestos tile.

Features of aqueous acrylic resins for carpet tile adhesives are:

- Water resistance
- Durability
- Specific adhesion to a variety of surfaces
- No solvent toxicity

Formulations for removable and permanent carpet tile adhesives are shown in Table 5.

**Floor Tile Adhesives.** Mastic floor tile adhesives are highly filled adhesive formulations designed for use in adhering vinyl and vinyl asbestos tile, wood parquet, carpet, and other flooring materials. The formulations in Table 6 can be used to join two nonporous substrates, provided the substrates are joined after the adhesive mastic has dried. If at least one porous substrate is involved, optimum bond strength can be obtained by joining the two surfaces in a wet laminating operation—that is, before the adhesive has dried. The viscosities of the three systems can, of course, be adjusted to meet specific needs. Lower RMC (raw material cost) formulations can be achieved, at some compromise in performance, by extending the pigment/binder ratio.

**Ceramic Tile.** Ceramic tile adhesives are highly filled adhesive mastics designed for ad-

**Table 6. Wet Mastic Floor Tile Adhesive—Permanently Pressure Sensitive.**

<i>Components<sup>a</sup></i>	<i>Parts by Weight</i>
Rhoplex N-580 (55% solids)	100.0
Water	1.8
Propylene glycol	3.0
Nopco NXZ	0.09
Triton X-405	2.5
Stabilite® ester #10/xylene (70/30)	76.7
Ammonium hydroxide (10%)	2.0
Gold Bond R Silica (300 mesh)	80.55
Acrysol ASE-60/water (1/1)	5.0
<i>Constants</i>	
Pigment/binder ratio	6/1
Rosin/binder ratio	1.5/1
Percent solids	71.7
Viscosity, Brookfield #4/0.3 rpm, cps	2,000,000
pH	8.0
Freeze/thaw stability, cycles	5

<sup>a</sup>A suitable biocide is recommended for in-can preservation.

hering tile to walls and floors. Even though these adhesives are highly filled, they still must exhibit a high degree of bond strength and water resistance along with desirable handling characteristics like ease of trowelability, sufficient open time, and long term storage characteristics. Ceramic tile adhesives based on Emulsion E-1997 (see Table 7) possess such desirable properties as smooth trowelability, wet adhe-

**Table 7. Ceramic Tile Adhesive—High Bond Strength.**

<i>Components<sup>a</sup></i>	<i>Parts by Weight</i>
Emulsion E-1997 (49% solids)	210.0
Propylene Glycol	10.0
Water	70.0
Tamol 731	5.0
Urea	30.0
Defoamer	1.0
Duramite Calcium Carbonate	500.0
Acramine Clear Concentrate NS2R	14.0
<i>Constants</i>	
Pigment/binder ratio	5/1
Percent solids	76.0
Approximate open time	15–30 min.
Storage stability, 1 month @ 50°C	Pass
Freeze/thaw stability	5+ cycles
ANSI #1, wet type	80 psi
Viscosity, TE/4, poise	600,000

<sup>a</sup>A suitable biocide is recommended for in-can preservation.

**Table 5.**

	<i>Removable</i>	<i>Permanent</i>
<i>Components, parts by weight</i>		
Rhoplex N-619 (high tack PSA)	—	100
Emulsion E-1791 (low tack PSA)	100	—
Acrysol ASE-60 (thickener)	0.75	0.8
Triton X-155 (surfactant)	—	0.3
<i>Physical Properties</i>		
pH	9.2	6.7
Viscosity (#4/20 rpm), cps	2000	5000
Solids, %	55	55

sion, low odor, adhesion to a variety of substrates and permanence of properties.

The ceramic tile adhesive shown in Table 7 is suitable for formulating an adhesive to meet ANSI Type I and II specifications. One can significantly reduce cost while still meeting ANSI requirements by modifying the ratios of the same ingredients to achieve a pigment/binder ratio of 6 to 1. Likewise, repositionability and open time may be extended by incorporating a plasticizer, such as Paraplex® WP-1, at a rate of 5 parts per 100 of polymer emulsion.

## ENGINEERING ADHESIVES

Engineering adhesives are solventless, liquid, reactive, durable adhesives for bonding durable substrates. There are six recognized chemical types of engineering adhesives: acrylic, anaerobic, cyanoacrylate, epoxy, silicone, and urethane. Strictly speaking, the first three in this list are varieties of acrylic, but only the first will be discussed here. There is, however, considerable overlap in the chemistry and properties of acrylic and anaerobic adhesives. Since considerable progress has been made in acrylic adhesives over the last two decades, those used in engineering applications are now referred to as "modified" acrylic adhesives.

### Chemistry and Technology

Early acrylic engineering adhesives were quite simple in composition and thus service well to illustrate their basic technology. An example of such an adhesive is as follows:

Component	Parts by Weight
1. Methyl methacrylate	85.0
Polymethyl methacrylate	15.0
N,N-Dimethyl aniline	0.5
2. Benzoyl peroxide	0.5

When its components are mixed the adhesive has a pot life of about one-half hour. The mixture is placed between adherends and allowed to polymerize via a free-radical mechanism. The free radicals are supplied from the decomposition of peroxide activated by dimethyl aniline. In effect, the adherends serve as the

reaction vessel for the polymerization of methyl methacrylate to a plastic with adhesion to the adherends.

*Modified* or second generation acrylic engineering adhesives are more complicated than those described above. In modified acrylic adhesives, polymerization between adherends leads to *impact resistant* plastics with adhesion to the adherends. The following formulation of Brigas and Muschiatti illustrates an early modified acrylic engineering adhesive:<sup>18</sup>

Component	Parts by Weight
Methyl methacrylate	85
Methacrylic acid	15
Ethylene glycol dimethacrylate	2
Chlorosulfonated polyethylene	100
Cumene hydroperoxide	6
N,N-Dimethyl aniline	2

The chlorosulfonated polyethylene separates into small rubber domains during polymerization of methyl methacrylate. These domains absorb fracture energy generated in the glassy poly(methyl methacrylate) under loading. Grafting between the rubbery and the glassy phases appears to be necessary to effect transfer of energy to the rubber.

A storage-stable, no-mix version, also called a two-part surface-activated version of the above is described in Ref. 18 as follows:

Component	Parts by Weight
Methyl methacrylate	85
Methacrylic acid	15
Ethylene glycol dimethacrylate	2
Chlorosulfonated polyethylene	100
Cumene hydroperoxide	0.4

In this example the aniline activator is replaced by a condensate of butyraldehyde and aniline which is applied to one or both adherends in a thin film prior to application of the adhesive. The activator generates a free-radical



flux on contact with the adhesive. This flux spreads across the adhesive layer to polymerize it. This phenomenon is unique to acrylic adhesives. A difficulty with this process is that the radical flux tends to die out with distance from the activator. Practical bond thickness is thus limited.

Another formulation of Toback and O'Connor<sup>19</sup> employs hydroxypropyl methacrylate as the fluidizing reactive component of a modified acrylic engineering adhesive. A condensation product of three moles of hydroxyethyl methacrylate, three moles of toluene diisocyanate, and one mole of a polypropylene triol provides a rubber phase.

W. A. Lees<sup>20</sup> has pointed out the difficulties of achieving the optimum particle size distribution of the precipitating rubbery phase. Moser and Slowik<sup>21</sup> have addressed this problem by using preformed rubbery domains of the type used in impact resistant plastics. Suitable impact improvers are described as core/shell polymers which have a crosslinked acrylic or butadiene-based elastomer graft-linked to an outer rigid thermoplastic polymer.

The following two formulations illustrate the effect of the impact improver. Both were polymerized between aluminum adherends which have been primed with a thin film of butyraldehyde and butylamine condensate.

Component	Parts by Weight	
	A	B
Butadiene-styrene/methyl methacrylate core/shell polymer	30	—
Hydroxypropyl methacrylate	60	77
Acryloxypropionic acid	10	14
Cab-O-Sil® (thickener)	—	9
Cumene hydroperoxide	2	3

Impact-modified formulation A gave 2,200 psi (15 MPa) lap tensile shear strength when tested by ASTM Method D-1002 and greater than 80 in.-lb (9 N m) of impact resistance as tested by ASTM G-17 falling weight method. The comparative formulation B gave 960 psi (6 MPa) shear and 20 in.-lb (2.3 N m) impact.

## Radiation Curing

The polymerization of the monomer in acrylic engineering adhesives can be initiated by electron beam or ultraviolet (UV) radiation, provided that the adherends or the fillers in the adhesives are not barriers to radiation. Acrylic monomers are generally more reactive to radiation than methacrylates. Electron beams generate free radicals directly in the adhesive, whereas UV curing requires a photosensitizer or photoinitiator to provide free radicals.

## Application Processes

Because of their reactivity, acrylic engineering adhesives are necessarily two-part adhesives. No special application equipment is required for the two-part surface activated type, which is also called the no-mix type. As mentioned earlier, it is only necessary to wipe the activator on to the surfaces before spreading the adhesive and mating the surfaces.

Two-part mixed-type acrylic adhesives are applied like two-part mixed epoxy adhesives with meter or meter-and-mix equipment. The two parts may be metered into a container for immediate mixing and application, or metered into a static mixer and immediately dispensed to the adherends to be joined. A simple illustration of meter-and-mix equipment is the double-barrel syringe, which delivers the two parts of the adhesive to a nozzle containing static mixing elements. These elements are alternating right and left hand helices connected off center to each other. At the other end of the complexity spectrum is the equipment for automated assembly lines.

## Current Uses

Modified or toughened acrylic adhesives have been used since the early 1980s to bond metal stiffening strips to the glass fiber-reinforced plastic window panels of rail cars.<sup>22,23</sup> There is a similar use in truck cab construction.<sup>24</sup> In another transportation use, an acrylic adhesive is used to bond the components of bodyside doors of freight locomotives.<sup>23</sup> These components are made of steel with a zinc coating. Adhesive bonding eliminates the surface blemishes of

spot-weld bonding. A two-part premix acrylic adhesive was the only one that met all of the requirements of manufacturing and use, namely, minimum surface preparation, fast cure, and resistance to impact, high humidity, water, and oil coolant.

General sheet steel bonding is done with acrylic adhesives.<sup>25</sup> Wood/aluminum sails of wind-powered electric generators are bonded

with an acrylic engineering adhesive.<sup>26</sup> Other uses are aircraft windshields, satellite antenna dishes, solar energy modules, outdoor signs, computer housings, and filtration screens.<sup>27</sup>

The use of a second generation two-part acrylic adhesive has allowed a sports car manufacturer to assemble a bumper which passes a five mile per hour impact.<sup>28</sup>

## APPENDIX

### Suppliers of Raw Materials Mentioned in This Section

Acramine Clear Concentrate NS2R

Acrysol thickeners

Balab 3056A

Camel Carb

Cellufloc

Cellulose Flock #CP-40

Composition T

Cymel

Dowper

Duralmite

Ethyene glycol

Foamaster

Formica

Gold Bond R Silica

Hi Sil 422

Methocel E-4M

Nopco NXZ

Pa. Limestone

Paraplex WP-1

Petinos Sand

Propylene glycol

Rhoplex acrylic emulsions

Robond acrylic resin

Stabelite Ester #10

Tamol dispersants

Texanol

Tide

Triton surfactants

Varsol

Vinol 540

Mobay Chemical Company

Rohm and Haas Company

Witch Chemical

Campbell Company

Georgia-Pacific Corporation

International Filler Corporation

Dow Chemical Company

American Cyanamid

Dow Chemical Company

Thompson, Weinman & Company

Eastman, Shell, Dow

Diamond Shamrock Corporation

American Cyanamid

Tammsco Inc.

PPG Industries, Inc.

Dow Chemical Company

Nopco Chemical Division

Pfizer

Rohm and Haas Company

Petinos Company

Ashland, Dow, Olin, Union Carbide

Rohm and Haas Company

Rohm and Haas Company

Hercules, Inc.

Rohm and Haas Company

Eastman

Proctor and Gamble

Rohm and Haas Company

Exxon

Air Products and Chemicals, Inc.

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# Anaerobic Adhesives

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## INTRODUCTION

Anaerobic adhesives are single-component liquids or pastes which can be stored for prolonged periods of time at room temperature in the presence of oxygen but harden rapidly to form strong bonds when confined between surfaces that exclude air. Researchers at General Electric identified the first anaerobic adhesive in the late 1940s.<sup>1</sup> They discovered that tetraethylene glycol dimethacrylate, oxygenated by heating at 60–80°C in the presence of bubbled air, remained liquid when cooled as long as aeration was maintained. However, when the air bubbling was discontinued or when the liquid was pressed as a thin film between glass microscope slides, rapid crosslinking occurred forming a solid polymeric material.

“Anaerobic Permafil,” as the oxygenated dimethacrylate became known, was marketed by General Electric with little success. The inherent instability of the material placed onerous restrictions on handling, packaging, and shipping. A solution to the stability problem was provided when the cumbersome oxygenation process was replaced by the addition of controlled amounts of cumene hydroperoxide.<sup>2</sup> The resulting formulation still necessitated the pres-

ence of oxygen to prevent polymerization, but the required amount was reduced to the point where air permeating through the walls of a small, half-filled polyethylene bottle was sufficient to maintain liquidity for one year at room temperature.

Cumene hydroperoxide-based formulations, being more stable than the previous oxygenated materials, were slower to polymerize between glass surfaces but exhibited rapid bond formation between certain metal surfaces. Early researchers had foreseen the utility of anaerobic adhesives in locking threaded fittings in place and sealing flanged metal parts, and in 1953, the American Sealants Company (later to become Loctite Corporation) was established to address those marketing opportunities.<sup>3</sup>

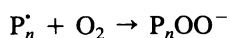
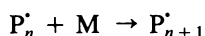
The first anaerobic adhesive, Loctite Sealant Grade A, was rapidly augmented by Grade C, a reduced strength product, and Grade D, a more viscous product. Surface primers were introduced to accelerate bonding between less reactive substrates. During the following 30 years, numerous additions and improvements to the product line were made. However, the basic advantages of anaerobic adhesives were evident from the outset. They offer the customer a method of assembly which simplifies

design and reduces costs by removing the need for intricate mechanical locking, sealing, and retaining devices. Anaerobic adhesives are easily applied and form bonds rapidly at room temperature. Bond strengths may be varied according to the wishes of the customer. The adhesives contain no solvents and material outside the bondline is readily removed. Extensions of anaerobic adhesive chemistry have made possible the development of porous metal sealants which improve machinability and strengthen castings, preapplied dry threadlocking and gasketing materials for additional convenience, and durable structural adhesives that do not require elaborate curing equipment.

## CHEMISTRY OF ANAEROBIC ADHESIVES

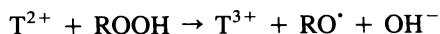
### Cure Systems and Stabilizers

The cornerstone of anaerobic adhesive chemistry is the set of competitive chemical reactions



in which  $P_n^{\cdot}$  denotes a free radical (an initiator fragment, or a propagating monomeric or polymeric species) and  $M$  is a vinylic monomer. Under conditions where the rate of formation of free radicals is low (absence of light, low temperature, etc.) and the concentration of oxygen is high, the tendency to polymerize is diminished. In the Permafil system the oxygenated resins underwent facile decomposition to form free radicals and large amounts of oxygen were required to react with these radicals and prevent polymerization. Since cumene hydroperoxide decomposes much more slowly, correspondingly fewer radicals are produced and less oxygen is required for stabilization. The enhanced reactivity of anaerobic adhesives on certain types of metal surfaces can be explained by the presence of transition metals on these surfaces. Transition metals undergo a one-electron transfer reaction with hydroperoxides to generate free radicals as shown in the

following reaction, where  $T$  represents a transition metal:



The desire to balance the reactivity and stability of anaerobic adhesives has led to a continuing search for compounds which accelerate the polymerization reaction without exerting a deleterious effect on product storability. Trialkyl amines were found to meet these criteria,<sup>4</sup> and were incorporated in the first generation of Loctite anaerobic products. Presumably the amine acted to polarize the hydroperoxide ions. This system remained sensitive to the nature of the substrate, curing rapidly on copper- and iron-rich surfaces and curing slowly or not at all on cadmium- or zinc-plated metals.<sup>5</sup> Subsequent research identified a coaccelerator combination, *o*-benzoic sulfimide (saccharin) and dialkylarylamines, which enhanced cure speeds on all surfaces.<sup>6</sup> Model studies suggest that gradual autoxidation of dialkylarylamines occurs during prolonged storage, causing a decrease in cure speed and emphasizing the importance of the amine in the polymerization process.<sup>7</sup> The same studies indicate that the amine reacts extensively with hydroperoxides only at elevated temperatures, demonstrating that the sulfimide plays an equally vital role in the initiation chemistry. Preformed sulfimide/amine salts have been used successfully to initiate acrylic polymerizations.<sup>8</sup> The presence of low levels of water appears to improve the performance of this cure system.<sup>9</sup>

Further improvements in the reactivity of anaerobic adhesives were obtained with the introduction of hydrazide accelerators.<sup>10</sup> However, incorporation of more active cure systems was made possible only by concurrent advances in stabilization chemistry. Early formulations employed quinone polymerization inhibitors which were effective at levels of 10–1000 parts per million.<sup>11</sup> As more active formulations were developed, attempts to combat premature polymerization by addition of greater quantities of inhibitor served only to reduce performance. A significant breakthrough occurred when a method of removing trace amounts of contaminant metals from anaerobic formulations was

devised.<sup>12</sup> The method consisted of treating the formulations with insoluble chelating agents which would reduce the iron content to a level of 100 parts per billion or less. Enhanced stabilities resulting from this treatment highlight once again the sensitivity of the free-radical generation process to minute concentrations of transition metals.

### Monomers and Resins

One of the principal limitations of the early anaerobic adhesives was the relative brittleness of the cured products.<sup>13</sup> In situations where high bond strengths were unnecessary, the problem could be alleviated by the addition of plasticizers. However, a more universally applicable solution required redesign of the polymerizable constituents of the adhesives. The structure of short-chain polyethylene glycol dimethacrylates results in rapid gelation during polymerization, leading to highly crosslinked networks consisting of relatively polar segments. An initial response to the brittleness problem involved replacing the polyethylene glycol segments between acrylic functions with segments derived from flexible hydrocarbons and diisocyanates.<sup>14</sup>

In various forms, this strategy has been pursued through numerous resin syntheses. Segments based on polytetramethylene glycol and hydrogenated bisphenol A were capped with diisocyanates and hydroxyalkylmethacrylates.<sup>15</sup> Increased flexibility was achieved by incorporating polybutadiene segments into similarly capped resins.<sup>16</sup> Other researchers demonstrated the utility of capping agents containing both the isocyanate and acrylic functions.<sup>17,18</sup> The variations in tensile strength, elongation, hardness, and tear strength for a model anaerobic adhesive based on methyl methacrylate and an acrylate-terminated butadiene/acrylonitrile elastomer are illustrated in a recent review article<sup>19</sup> and are ascribed to the formation of discrete rubbery and glassy domains within the cured polymer matrix.

Attempts have been made to introduce polymerizable functionalities other than acrylic into anaerobic adhesives. Monoacrylates have been described which also contain internal

chain unsaturation with the object of providing secondary curing sites for improved heat resistance.<sup>20</sup> Anaerobically curable adhesives based solely on trifunctional allylic monomers have also been proposed,<sup>21</sup> but the vast majority of the commercially available products still employ acrylic monomers and resins.

## FORMULATING FOR APPLICATIONS

### Primers

In situations where the rate of assembly demands extremely rapid cure times, or where the surfaces to be bonded are inherently unreactive, treatment of substrates with a primer is often necessary. Primers consist of compounds which accelerate the curing reactions. Since they would destabilize the adhesive if added directly to the formulation, they are supplied and used as a separate component. The criteria for an acceptable primer include compatibility with the adhesive, the ability to accelerate the rate of curing, and lack of any adverse effects on bond strengths. Various thiazoles,<sup>22</sup> butyraldehyde-aniline adducts,<sup>23</sup> and thioureas<sup>24</sup> were found to meet these criteria. Since trace levels of transition metals accelerate anaerobic adhesive cure, primers containing complexed copper have been employed successfully.<sup>25</sup> In another system, acidic primers are used which react with ferrocene in the adhesive to release the required metal ions.<sup>26</sup>

Primers are typically supplied as dilute solutions in nonflammable, nontoxic solvents and applied by spraying or brushing onto the substrate.

### Microencapsulation of Curatives

An ingenious technique for separating a particularly active component of a cure system from the bulk of the adhesive is to enclose particles of the compound inside a minute, thin-walled shell, or microcapsule, which can then be ruptured at a desired time to release the contents. This technique forms the basis of preapplied dry threadlocking materials.<sup>27</sup> Such materials are cast as dry films on threaded fittings and the coated parts are storable for long periods of time. The act of assembling with the threaded

fastener causes rupturing of the microcapsules and activates the threadlocking formulation.

A recent variation of the microencapsulation technique involves separating the components of the cure system by immobilizing the entire anaerobic adhesive formulation within a low-melting-point wax.<sup>28</sup> The wax slurry can be applied at relatively low temperatures in the presence of oxygen and allowed to solidify in the threaded area of a fastener. Assembly with the attendant exclusion of oxygen mixes the components and initiates the curing process.

### Fillers

Certain applications, e.g., porous metal sealing, require an anaerobic adhesive to be a thin, free-flowing liquid. However, other applications, such as gasketing, involve filling relatively large gaps. Under these conditions, an adhesive which does not flow or sag is desirable. The addition of powdered polyethylene fillers renders the organic resin base thixotropic in nature.<sup>29</sup> Thixotropic adhesives have also been formulated using self-structuring silica fillers. The resulting gasketing materials can be applied from tracing lines of caulking guns, or screen printed through fine mesh stencils.

### Plasticizers and Thickeners

One of the earliest and most enduring demands voiced by users of anaerobic adhesives was for a graded product series of different viscosities and ultimate strengths. Modification of these physical properties is readily accomplished with the aid of thickeners or reactive diluents, which raise or lower the viscosity of the organic resin base, and nonreactive plasticizers, which lower the bond strength of the fully cured product. Examples of commonly used thickeners are polyester resins, polystyrene and polyalkyl acrylates and their copolymers, and polybisphenol A maleate. The principal reactive diluents are low molecular weight monofunctional acrylates. Traditional plasticizers include poly(ethylene glycol) octanoates.

A key factor in selecting any additive for an anaerobic adhesive formulation is the effect which that additive exerts on the delicate balance between activity and stability. Additives

must be carefully analyzed for the presence of trace levels of contaminants which could impair the performance of the product.

## COMMERCIALLY AVAILABLE ANAEROBIC ADHESIVES

Tables 1–4 list selected commercially available anaerobic adhesive products, illustrating the variety of uncured and cured physical properties which results when formulations are tailored to meet specific application needs. Many products are color-coded for easy recognition and on-part identification.

## HANDLING TECHNIQUES

### Health and Safety

Most anaerobic adhesive formulations are based on oligomeric acrylic esters, inherently low-toxicity materials. Various formulations contain additives such as adhesion promoters or cure components, and after excessive or repeated skin contact may cause skin irritation in sensitive persons. Adhesives should be washed away with water after skin contact. Nonaqueous hand cleaners assist in removal of adhesive. Skin contact should be avoided by the use of appropriate application equipment.

One indication of the relatively innocuous nature of anaerobic adhesives is the fact that products such as Loctite Pipe Sealants 567 and 592 have been recognized by the U.S. Department of Agriculture as being chemically acceptable for use on meat or poultry processing machinery. Primers normally contain volatile solvents and should be used only in well ventilated environments.

### Packaging

Anaerobic adhesives are formulated with cure components and stabilizers balanced so as to maintain storability under proper conditions for at least one year at room temperature. Storage at higher temperatures leads to correspondingly shorter product lifetimes by accelerating the free radical polymerization process. Exposure to strong light for prolonged periods of time also has an adverse effect on storability. Consequently, anaerobic adhesives are packaged in

**Table 1. Selected Commercially Available Anaerobic Adhesives: Threadlocking.**

<i>Application</i>	<i>Trade Name/ Product No.</i>	<i>Color</i>	<i>Gap-Filling Ability, mm</i>	<i>Viscosity, mPa·s (mean)</i>	<i>Torque, N·m, Breakaway/ Prevailing</i>	<i>Cure Speeds at Room Temperature</i>	
						<i>w/o Primer, Fixture/Full</i>	<i>w/Primer, Fixture/Full</i>
Preapplied; high strength	Dri-Loc/200	yellow	—	—	25/12	10 min/72 hr	—/—
Preapplied; medium strength	Dri-Loc/202	green	—	—	23/12	10 min/72 hr	—/—
Preapplied; mild strength	Dri-Loc/203	silver	—	—	19/85	10 min/72 hr	—/—
Small screws; low strength	222	purple	0.13	1000	4.5/2.5	20 min/24 hr	5 min/24 hr
General purpose; medium strength	242	blue	0.13	1000	7/4	20 min/24 hr	5 min/6 hr
Large bolts; high strength	262	red	0.13	1500	21/18	20 min/24 hr	5 min/6 hr
Gap-filling; high strength	271	red	0.18	500	18/25	20 min/24 hr	5 min/6 hr
High-temperature resistance	272	red	0.18	7000	17.5/27	30 min/24 hr	5 min/24 hr
High viscosity	277	red	0.25	6500	12/17	60 min/24 hr	10 min/2 hr
Low viscosity	290	green	0.10	12	7/22.5	10 min/2 hr	—/—

*Note:* All products listed function satisfactorily over the temperature range -55 to 150°C (-65 to 300°F) except for 272, which has an upper temperature limit of 232°C (450°F).



**Table 2. Selected Commercially Available Anaerobic Adhesives: Sealing.**

<i>Application</i>	<i>Trade Name/ Product No.</i>	<i>Color</i>	<i>Gap-Filling Ability, mm</i>	<i>Viscosity, mPa·s (Mean)</i>	<i>Temperature Range, °C (°F)</i>	<i>Cure Speeds at Room Temperature</i>	
						<i>w/o Primer, Fixture/Full</i>	<i>w/Primer, Fixture/Full</i>
General purpose thread sealing	Pipe Sealant with Teflon/592	White	0.50	200,000	-55 to 204 (-65 to 400)	24 hr/72 hr	15 min/5 hr
Fluid power sys- tem connections	Hydraulic Sealant/569	Brown	0.13	400	-55 to 150 (-65 to 300)	45 min/2 hr	—/—
General purpose gasketing	Gasket Elimina- tor/515	Purple	unprimed 0.25 primed 1.25	350,000	-55 to 150 (-65 to 300)	1 hr/12 hr	15 min/2 hr
High temperature gasketing	Gasket Elimina- tor/510	Red	unprimed 0.25 primed 0.50	350,000	-55 to 204 (-65 to 400)	4 hr/12 hr	30 min/4 hr
Large gaps, instant seal	Gasket Elimina- tor/504	Orange	0.75	1,500,000	-55 to 150 (-65 to 300)	30 min/12 hr	—/—

**Table 3. Selected Commercially Available Anaerobic Adhesives: Retaining.**

<i>Application</i>	<i>Trade Name/ Product No.</i>	<i>Color</i>	<i>Gap-Filling Ability, mm</i>	<i>Viscosity, mPa·s (mean)</i>	<i>Shear Strength DaN/cm<sup>2</sup> (steel)</i>	<i>Cure Speeds at Room Temperature</i>	
						<i>w/o Primer, Fixture/Full</i>	<i>w/Primer, Fixture/Full</i>
General purpose	RC/601	green	0.13	100	210	10 min/1-6 hr	5 min/20 min
High temperature	RC/620	green	0.13	7000	210	30 min/8-10 hr	5 min/8-10 hr
High strength	RC/680	green	0.38	2000	280	30 min-4-6 hr	5 min/4-6 hr

*Note:* All products function effectively over the temperature range -55 to 150°C (-65 to 300°F) except for RC/620, which has an upper temperature limit of 232°C (450°F).

Table 4. Selected Commercially Available Anaerobic Adhesives: Bonding.

Application	Trade Name/ Product No.	Color	Gap-Filling Ability, mm	Viscosity mPa·s (Mean)	Shear Strength, DaN/cm <sup>2</sup> (steel)	Cure Speeds at Room Temperature	
						w/o Primer, Fixture/Full	w/Primer, Fixture/Full
High impact, peel strength	Steelbonder/ 324	dark amber	1.00	18,000	300	—/—	3 min/24 hr
Environmental resistance	Speedbonder/ 325	dark amber	1.00	20,000	180	—/—	5 min/24 hr
Rapid curing	Speedbonder/ 326	amber	0.50	12,000	225	—/—	2 min/24 hr

pigmented containers which act as barriers to light.

The most stringent packaging requirements arise as a result of the need for a constant supply of oxygen. Consumption of oxygen by anaerobic adhesives is a continuous process. Therefore, package design must facilitate contact of all parts of the adhesive with air. Storage stability is significantly higher in thin-walled containers than in thick-walled containers, in low density polyethylene containers rather than in high density polyethylene, and in small containers rather than large.

An ingenious solution to the problem of generating a high surface area-to-volume ratio in thin-walled containers while maintaining the structural integrity of the package during handling was devised recently.<sup>30</sup> This solution involves constructing a rigid plastic framework surrounding and supporting a soft, flexible, accordionlike package which lends itself to easy product dispensing.

### Dispensing Equipment and Application Techniques

Continuous assembly operations entail precise metering and application of anaerobic adhesives. Automated systems have been designed to cope with a wide range of end uses, from dispensing threadlockers onto small fasteners to impregnating large porous metal castings with sealant. These systems play an essential role in augmenting the cost reductions obtained through the use of anaerobic adhesive products by eliminating material waste, shortening cycle times, and reducing labor.

One of the earliest and simplest applicators was based on a peristaltic pump mechanism which enabled amounts of adhesive varied by a screw adjustment from 0.01 ml to 0.04 ml to be dispensed.<sup>31</sup> Most current liquid dispensing systems employ air pressure to force adhesive through feed lines which are regulated by pinch valves, diaphragm valves, or solenoid valves. The adhesive is then dispensed onto the substrate through handguns, spring-loaded needle tips, or custom applicator heads designed to match the contours of the substrate. Threadlocking and sealing formulations can also be applied simultaneously to large num-

bers of threaded parts by tumbling the parts together with a small amount of the formulation.

Gasketing products are usually viscous and often thixotropic. Intricate patterns can be laid down rapidly either by programmable tracing lines or by screen printing through precut stencils. Anaerobic materials lend themselves to screen printing since they do not cure or dry out when spread thinly on the mesh.

More elaborate equipment is necessary for vacuum impregnation. In a typical process, parts are suspended in a basket over liquid resin inside a vessel. The vessel is then evacuated to remove air from the porous structure of the parts. The basket of parts is then lowered into the resin and the vessel is repressurized, forcing sealant into the pores and cracks in the parts. Excess sealant is removed by centrifugation and the cure process is completed in a warm water wash.

Obviously, successful application equipment design is contingent upon incorporation of materials compatible with anaerobic adhesives. Components or fittings should be fabricated from materials which do not contain destabilizing components.

## APPLICATIONS AND PERFORMANCE DATA

### Threadlocking

The first mechanical design problem to be solved with the aid of anaerobic adhesives was the problem of loosening or unwinding of threaded metal fasteners under periodic overload which makes the threads slide sideways. This condition is commonly encountered in fasteners which are subjected to vibration. The effectiveness of anaerobic threadlocking adhesives is demonstrated by transverse shock and vibration experiments in which nut-and-bolt assemblies are struck repeatedly at right angles by air hammers. Results from these experiments, illustrated in Fig. 1, show that assemblies treated with chemical threadlockers resist the unwinding forces associated with lateral movement. Most conventional mechanical locking methods fail this stringent test.<sup>32</sup>

In addition to vibration resistance, threadlocking adhesives provide the user with the

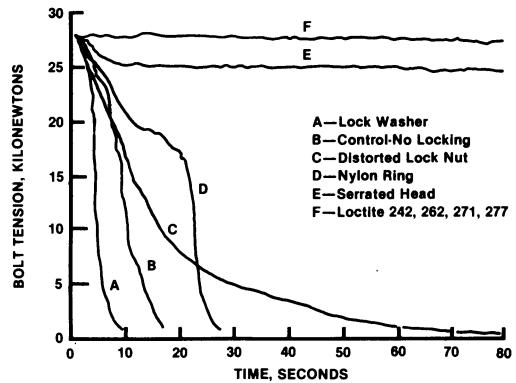


Fig. 1. Effectiveness of various threadlocking methods in preventing loosening of  $\frac{3}{8}$ "-16 bolts during transverse shock and vibration testing.

ability to establish predetermined values of breakaway torque (the torque needed to move a tightened fastener), prevailing torque (the resistance to further movement after the initial movement), and torque tension (the force which clamps the mated parts together). Commercially available threadlocking products are graded according to their breakaway and prevailing torques on standard nut-and-bolt assemblies. Figs. 2-5 illustrate the performance of a typical anaerobic threadlocking adhesive, Loctite 242, on a variety of such assemblies.

In practice, anaerobic chemical threadlockers are used in areas as diverse as typewriter screws, carburetor adjusting screws, railroad

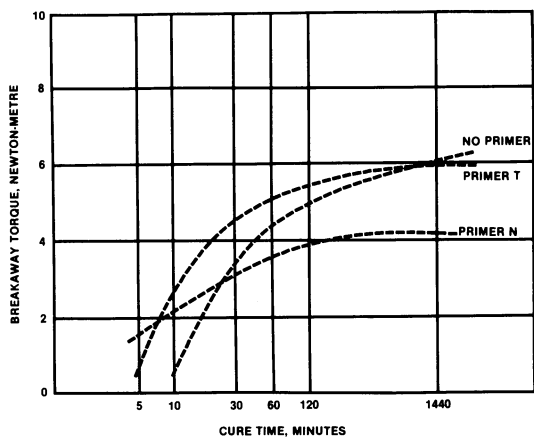


Fig. 2. Strength development of Loctite 242 cured with different primers on "as received" steel  $\frac{3}{8}$ "-16 nuts and bolts.

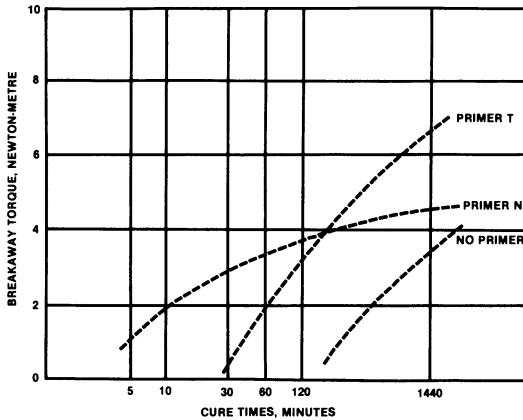


Fig. 3. Strength development of Loctite 242 cured with different primers on cadmium-plated  $\frac{3}{8}$ "-16 nuts and bolts.

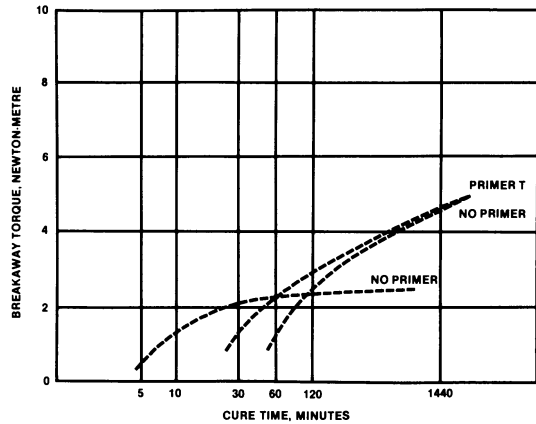


Fig. 5. Strength development of Loctite 242 cured with different primers on zinc-plated  $\frac{3}{8}$ "-16 nuts and bolts.

bolts on wear plates, hydraulic line fittings, and bulldozer track bolts.

### Sealing

Two major application areas in which anaerobic sealants have had a profound impact are porous metal impregnation and liquid gasketing. Although the physical properties of the products directed at these areas are extremely dissimilar in the uncured state, the cured materials share common features which render them uniquely suitable as sealants. Both types of product cure to form materials which resist attack by most industrial fluids, counterbalance the effects of surface imperfections, and do not shrink or crack during cure.

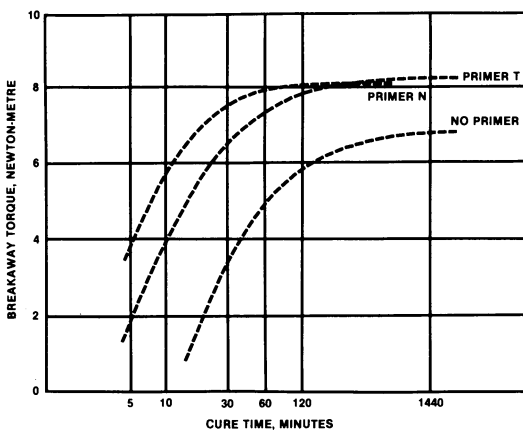


Fig. 4. Strength development of Loctite 242 cured with different primers on phosphate/oil  $\frac{3}{8}$ "-16 nuts and bolts.

Impregnation sealants are very low viscosity liquids which, when simply painted onto a surface or applied under vacuum as described earlier, migrate into pores, cracks, and surface imperfections in castings, welds, or powdered metal parts. Anaerobic sealants have replaced older types of sealant because of the relative ease and cleanliness of their application. Cure occurs only where desired and excess resin is easily removed. Castings sealed with the resins exhibit improved mechanical properties. One of the most impressive benefits of the impregnation process is the improvement in machinability which results from the smoothing of surfaces due to the filling of voids and crevices.

Anaerobic gasketing products are highly viscous thixotropic pastes. These characteristics minimize the tendency to sag or migrate and maximize gap-filling ability. Although typical liquid gasketing products may take several hours to develop fully cured properties (see Fig. 6), products such as Loctite Gasket Eliminator 504 are formulated to provide instant pressure seals even at relatively large gaps (Fig. 7). Such products find uses in transmission housings, pumps, thermostats, axle covers, and compressors. In certain cases, liquid gaskets are used to coat conventional gaskets and provide resistance to deformation.

### Retaining

Designers of cylindrical assemblies such as bearings or gears have traditionally relied upon

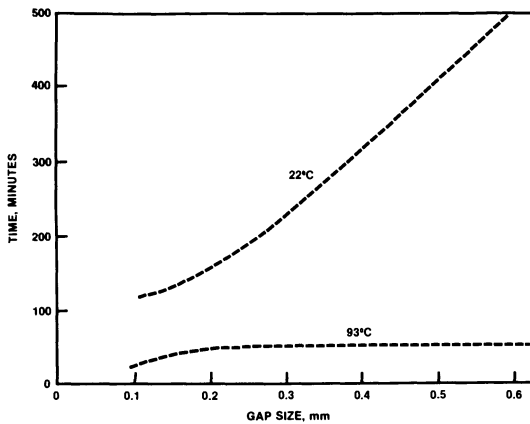


Fig. 6. Time to full cure of Loctite Gasket Eliminator 504 on steel flanges without primer.

interference fits to provide structural integrity. However, even carefully machined components have a relatively low metal-to-metal contact area. Consequently, pushoff strengths are reduced. Anaerobic retaining compounds fill the voids between the two surfaces, augmenting the mechanical action of the interference fit. In cases where slip-fitted or worn parts are used, retaining compounds provide structural integrity where none would otherwise exist.

Retaining adhesives have been formulated which exhibit improved bond strengths when subjected to high temperatures. For example, Loctite Retaining Compound 620 develops a 50% increase in shear strength when bonds are heated to 149°C for 2000 hours and tested at that temperature. Prolonged heating at 204°C

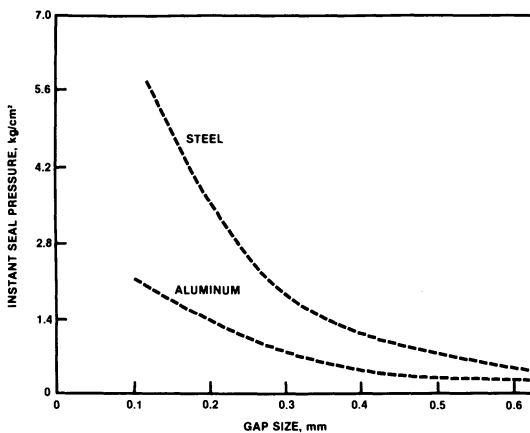


Fig. 7. Sealing ability of Loctite Gasket Eliminator 504 on nine 5-mm flanges measured immediately after assembly.

produces a smaller increase. Even after 2000 hours at 232°C, bonds assembled with this product maintain 75% of their initial strength.

### Structural Bonding

The application areas into which anaerobic adhesives have made their most recent inroads are those in which the adhesive is used to assemble flat, structurally bonded parts. Impetus for the replacement of more conventional structural adhesives by anaerobic products can be attributed to the ease of use, lack of mixing or pot-life problems, reduced toxicity, and rapid cure associated with the anaerobic materials. The incorporation of novel synthetic resins has extended the range of properties available in cured anaerobic adhesives, leading to improvements in tensile strength, impact strength, and peel strength. Primers or heat can be used to accelerate cure when necessary.

Table 5 contains a brief outline of results from physical property tests conducted on a

**Table 5. Physical Properties of Cured Loctite Speedbonder 324.**

<i>Test Results</i>		
Bond Thickness, mm	0.05	0.50
Test		
Tensile Shear Strength, DaN/cm <sup>2</sup> (ASTM D-1002-65)		
Aluminum	230	250
Steel	225	300
Impact Strength, J/cm <sup>2</sup> (ASTM D-950-54)	2.1	7.3
T-Peel Strength, kN/m (ASTM D-1876-61)		
Aluminum	5	—
Steel	10	8
<i>Bulk Properties</i>		
Coefficient of linear thermal expansion, 10 <sup>-5</sup> cm/cm/°C		12.6
Thermal conductivity, W/m-°K		0.12
Dielectric strength, V/mm		34,000
Volume resistivity, 10 <sup>12</sup> ohm-cm		3
Dielectric constant		
100 Hz		5.5
1 kHz		5.3
1 MHz		5.5
Dissipation factor		
100 Hz		0.039
1 kHz		0.033
1 MHz		0.045

typical anaerobic structural adhesive, Loctite Speedbonder 324. Unlike older anaerobic adhesives, products based on functionally designed resins exhibit bonding performance at 0.5 mm gaps which is at least as good as the zero-gap performance. This balance of properties has qualified anaerobic adhesives for structural bonding of dissimilar substrates in automotive glass to metal, loudspeaker magnets, firearm components, and decorative wood to cutlery applications.

## RECENT ADVANCES

### Surfactant Resins

One of the benefits of anaerobic impregnation sealants has been the comparative cleanliness of the processes in which they are used. The original anaerobic products were soluble in their uncured state in aqueous rinsing solutions which facilitated removal of excess material. Novel formulations have now been developed which incorporate surface active agents.<sup>33</sup> These formulations require only a plain water wash to remove uncured material, reducing operating costs and waste disposal.

### Dual-Cure Systems

In certain bonding applications, it is desirable to combine the benefits of single-component anaerobic adhesives with another cure mechanism which provides instant, though less durable, strength. For example, formulations have been developed which contain conventional anaerobic cure components and free-radically polymerizable monomers as well as tackifying resins which impart pressure-sensitive adhesion.<sup>34</sup> Materials based on this combination of cure systems exhibit immediate adhesion but permit repositioning before the slower anaerobic cure to a high strength bond occurs.

Another bonding method which allows rapid assembly and gradual development of bond strength hinges on a combination of anaerobic and ultraviolet light curing.<sup>35</sup> In the attachment of small electronic components to printed circuit boards, drops of adhesive are dispensed onto the board. Each component is then placed on top of the drops so as to form a fillet around

the edges of the component as well as a layer of adhesive underneath. Exposure to ultraviolet radiation causes the fillet to harden, immobilizing the component and permitting the slower anaerobic cure to proceed underneath.

### Ultraviolet Light Priming

Instead of directly curing an adhesive, ultraviolet light can replace chemical primers for anaerobic formulations under certain conditions.<sup>36</sup> This technique involves applying the formulation to a substrate and irradiating the coated substrate for a prescribed length of time. Although the adhesive remains liquid, it has become susceptible to anaerobic polymerization and assembly leads to bond formation.

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# Cyanoacrylate Adhesives

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Alkyl cyanoacrylate adhesives are unique among the many classes of adhesives, in that they are the only single component, instant bonding adhesives that cure at ambient conditions without requiring an external energy source. This characteristic, coupled with an ability to bond a wide variety of diverse and dissimilar substrates, has made them the ideal adhesives for numerous bonding applications. Though moderately high in bulk cost, they are very economical to use in practice because generally only one drop is required per bond and the nearly instantaneous room temperature cure makes fixtures, ovens, and expensive radiation sources unnecessary.

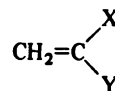
These compounds were first synthesized in 1947 by Alan Ardis<sup>1,2</sup> of B. F. Goodrich, who reported "hard clear glasslike resins" when heat cured. Their adhesive properties remained undiscovered until the early 1950s, when scientists at Eastman Kodak inadvertently bonded the prisms of an Abbe refractometer together while characterizing a cyanoacrylate monomer.

The first commercial result of the cyanoacrylate research work was Eastman 910®, a methyl ester based adhesive which was introduced in 1958. First thought to be an interesting, expensive curiosity, the new adhesive gradually began to build a unique and substantial niche for itself when used for bonding small parts that were difficult to assemble with conventional adhesives, or by mechanical means. Today over 1000 tons of various cyanoacrylate

adhesives are sold worldwide. Most are used for single drop applications. While numerous cyanoacrylate esters have been prepared, only a relative few are of significant commercial interest (Table 1). Today ethyl esters account for over 90% of the commercial volume because of a combination of superior bonding properties, long shelf life, and efficient production processing. The cure speed and adhesive strengths both tend to drop with increasing alkyl chain length. While the methyl volume continues to decrease, the allyl ester is now being aggressively marketed as a crosslinking, thermally resistant grade and alkoxyl-alkyl esters are beginning to find application as low odor—low bloom variations.

At present, there are six major producers of cyanoacrylate adhesives in the world: The Loctite Corporation and National Starch (Perma-bond) in the United States; Henkel AKG in Germany; Toa Gosei, Sumitomo, and Alpha Techno in Japan.

The reactivity of cyanoacrylates is directly traceable to the presence of two strong electron withdrawing groups (designated X and Y)



where X = CN  
Y = COOR

These groups make the double bond highly susceptible to attack by weak bases. Not all elec-



Table 1. Properties of Common Cyanoacrylate Monomers.

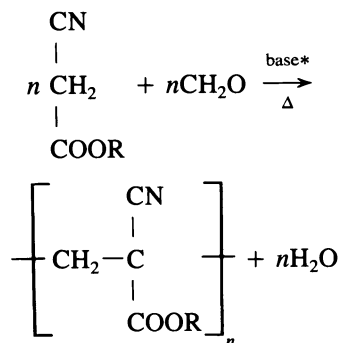
	Methyl	Ethyl	Isopropyl	Allyl	Butyl	Isobutyl	Methoxy Ethyl	Ethoxy Ethyl
Appearance								
Odor	very sharp, lachrymatory	sharp acrylic odor, lachrymatory	sharp acrylic odor, lachrymatory	sharp acrylic odor, lachrymatory	sharp acrylic odor, lachrymatory	sharp acrylic odor, lachrymatory	virtually odorless	virtually odorless
Viscosity, cps	2.2	1.9	2.1	2.0	2.1	2.0	2.6	5.0
Density	1.10	1.05	1.01	1.05	0.98	0.99	1.06	1.07
Boiling point, °C	48-49	54-56	53-56	78-82	83-84	71-73	96-100	104-106
mm Hg	2.5-2.7	1.6-3.0	1.0-2.5	6.0	3.0	1.9-2.2	2.6-3.3	5.0
Refractive index	1.4406	1.4349	1.4291	1.4565	1.4330	1.4352	-	1.4470
Heat of polymerization, kcal/mole	13.8	13.9	16.2	15 ± 1	15 ± 1	16.0	-	-
Flash point, °F	181	181	-	180	185	199	-	265

tronegative groups produce monomers that act like adhesives. Molecules of this type that show adhesive characteristics include: alkyl-2-cyanoacrylates,<sup>3</sup> the dialkyl methylene malonates,<sup>4,5</sup> the acyl-acrylonitriles,<sup>6</sup> and certain  $\alpha$ -substituted vinylidene alkyl sulfinates and sulfoxides.<sup>7</sup>

## SYNTHESIS OF ALKYL-2-CYANOACRYLATES

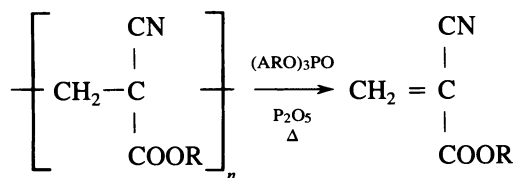
Two synthetic routes were employed by Alan Ardis in 1947.<sup>1,2</sup> The first route<sup>1</sup> involved the pyrolysis of an alkyl-3-acyloxy-2-cyanopropionate to yield an alkyl-2-cyanoacrylate plus a carboxylic acid.

The second and today most commercially favored method involves the Knoevenagel condensation reaction<sup>2,8</sup> of an alkyl cyanoacetate with formaldehyde in the presence of a base<sup>1</sup> to yield a poly(alkyl-2-cyanoacrylate) as follows:



Where B represents a basic end group. This reaction is usually carried out in a nonaqueous organic solvent to facilitate the removal of water from the system and to dissipate the heat evolved during the reaction exotherm.<sup>8</sup>

The polymerized cyanoacrylate is then heated to a temperature of 140–260°C, forcing the depolymerization of the polycyanoacrylate back to a cyanoacrylate ester:



\*e.g., piperidine.

In batch-type operations, yields in excess of 80% should be readily attainable. For this reaction to occur smoothly without repolymerization of the monomer, the basic catalyst from the first reaction must have been neutralized by the addition of a small amount of an acidic compound, e.g., phosphoric anhydride, etc.<sup>2</sup> In addition, a free radical inhibitor such as hydroquinone, catechol, etc.<sup>2</sup> should be added to the system to prevent repolymerization initiated by the formation of free radicals at the elevated temperatures. An anionic stabilizer such as  $\text{SO}_2$  must also be added to the fresh monomer to prevent subsequent polymerization.

Continuous processes for depolymerization of alkyl-cyanoacrylates have been proposed.<sup>9,10</sup> A more recent patent,<sup>11</sup> discusses carrying out the initial polymerization in an extruder in which gaseous by-products are removed in a degassing zone. The mother polymer produced is then mixed with hydroquinone and phosphorous pentoxide in a stream of  $\text{SO}_2$  to produce a stabilized methyl cyanoacrylate.

## STABILIZERS AND INHIBITORS

Cyanoacrylate monomers are highly reactive compounds and will polymerize via anionic and/or free radical mechanisms. The anionic reaction route is by far predominant and can be initiated by even small amounts of a weak base such as water. Exposure to extended high temperatures, ultraviolet light, or heat in the presence of peroxides can cause free radical polymerization to be initiated. The extreme anionic reactivity of these monomers was unobserved by early workers, probably due to crude preparatory methods which resulted in very impure, overstabilized product. Early attempts to polymerize the monomers nearly always involved thermal methods. It was not until the early 1950s that Coover and Shearer<sup>3</sup> of Eastman Kodak, using purer material stabilized with  $\text{SO}_2$  gas, discovered the unique polymerization and bonding characteristics of the cyanoacrylate monomers.

Inhibitors of both anionic and free radical polymerization are essential to maintain a usable shelf life for cyanoacrylate adhesives. Coupled with advances in manufacturing processes to

produce cleaner products, and the development of packages with improved barrier properties, today's stabilizer systems can provide cyanoacrylates with shelf lives of several years.

## Anionic Inhibitors

Since the anionic cure of cyanoacrylates proceeds as a result of basic catalysis, acids should naturally be considered as stabilizers. Acids of either the Lewis or protonic types have been used successfully.

Acidic gases such as  $\text{NO}$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{BF}_3$ , and  $\text{HF}$  have the advantage of stabilizing the monomer in both the liquid and gaseous phases.<sup>3,12,13</sup> This is useful in process distillation as it prevents premature polymerization of unstabilized monomer in distillation columns; at the same time, these acid gases also prevent the buildup of popcorn polymer in the head space of partially filled user packages.

Strong protonic acids such as aliphatic and aromatic sulfonic acids<sup>14</sup> and mineral acids have also been used in low levels as stabilizers. Combinations of nonvolatile sulfonic acids with gaseous stabilizers have been reported to offer synergistic effects.<sup>15</sup> Carboxylic acids and anhydrides have also been reported as stabilizers but generally are less effective than the stronger acids.

Acid strength and level are important variables in choosing a stabilizer. High levels of acid can overstabilize and make polymerization or cure speed of the adhesives quite sluggish and can contribute quite significantly to a rapid deterioration in adhesive performance. Despite the fact that water is known to be the most common initiator of cure, it has been shown that cyanoacrylates can and do contain surprisingly high levels of free water (up to several thousand ppm). The water, in combination with the strong acid stabilizer, can cause hydrolysis of the monomer, forming carboxylic acids which drastically retard cure speed. Therefore, the lowest level of acid requisite with adequate shelf life is most desirable.

Other compounds have also been reported as effective anionic polymerization inhibitors. Organic sulfur compounds when added to the prepolymer slurry in the manufacturing process before cracking or depolymerization have been

reported to yield stabilized monomer. These compounds include alkyl sulfates, sulfones, sulfoxides, sulfites, and 3-sulfolene.<sup>16</sup> Boric acid chelates have been reported<sup>17</sup> as have trimethyl silyl derivatives of sulfonic acids.<sup>18</sup> Imidazole adducts with SO<sub>2</sub> have also been reported as latent sources of SO<sub>2</sub> in cyanoacrylate adhesives.<sup>19</sup>

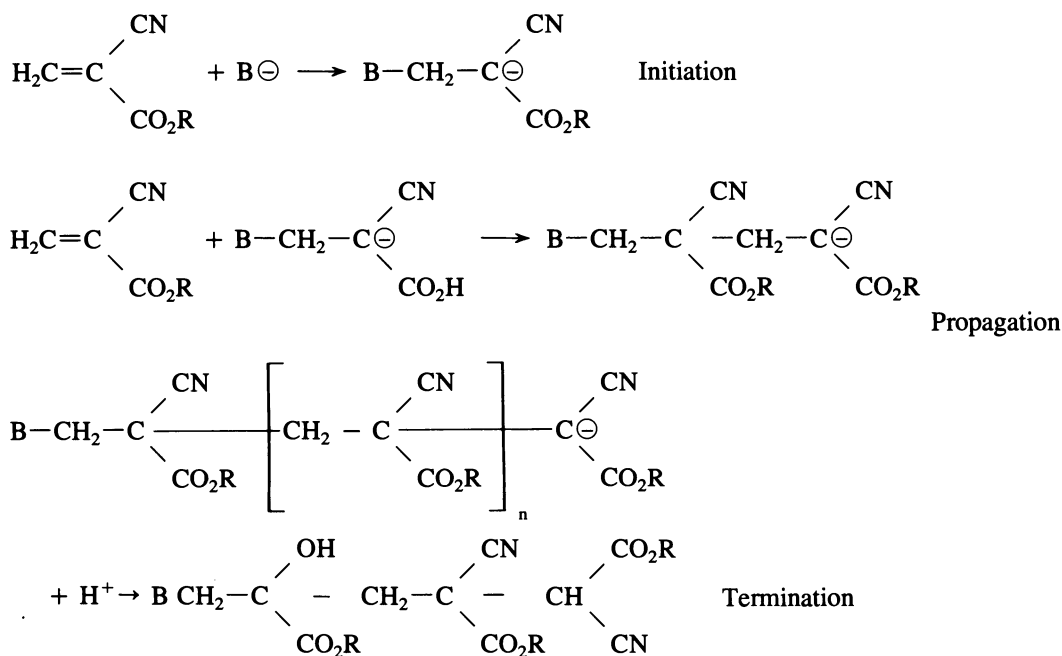
### Free Radical Stabilizers

As a rule, free radical stabilizers have only a minimal effect on the anionic polymerization

often is, relatively high. Levels of free radical stabilizers can range from 100 to several thousand ppm with little or no effect on the cyanoacrylate adhesives cure properties.

### CHEMISTRY OF POLYMERIZATION

As previously mentioned, alkyl-2-cyanoacrylates polymerize rapidly by an *anionic mechanism*<sup>20</sup> in the presence of weak bases at ambient temperatures. The reaction is highly exothermic. The actual polymerization can be depicted as follows:



rate, hence the selection of the type and concentration is not as critical as with the anionic stabilizer. The most common inhibitor used is hydroquinone, although quinone, a methyl ether of hydroquinone, and methoxy hydroquinone have been reported. Hindered phenols such as catechol, pyrocatechol, etc., have also been used with little or no advantage apparent over hydroquinone.

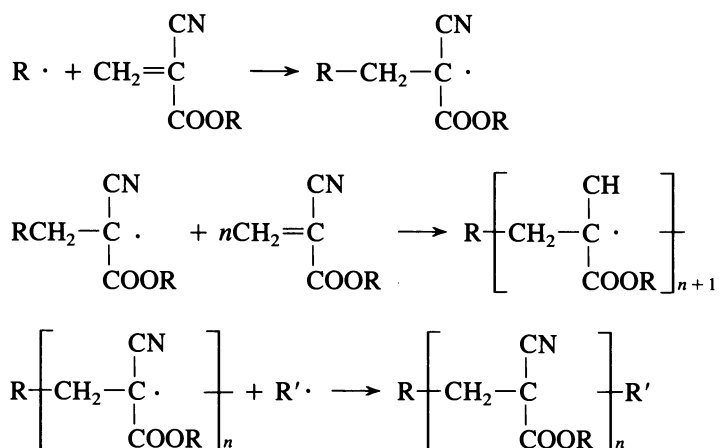
Since the predominant cure mechanism of cyanoacrylates is anionic, the level of free radical stabilizer which may be added to stabilize against heat or UV induced gelation can be, and

This reaction will continue until all available monomer is consumed or until growth is interrupted by the presence of an acidic species. It is the highly electronegative characteristics of the nitrile (—CN) and alkoxy carbonyl (—COOR) groups that account for the high reactivity of the double bond in the monomer such that weak bases as alcohol and water initiate rapid polymerization. In general, relatively low molecular weight chains are formed via this mechanism.

Since virtually all materials have a thin layer of moisture adsorbed onto their surfaces, it is easy to explain the reactivity of the alkyl-2-cy-

anoacrylates as perceived by the user. When a thin film of cyanoacrylate adhesive is spread onto a surface for bonding purposes, polymerization occurs rapidly as carbanions are generated at a very rapid rate as a result of the contact between the adhesive and adsorbed water molecules. The water molecules' hydroxyl groups effectively act to initiate polymerization. Since only thin films of cyanoacrylate are involved, complete polymerization through the bond line is extremely rapid, resulting in near instantaneous "fixturing" of parts.

When alkyl-2-cyanoacrylates polymerize via a free radical mechanism, the following reaction sequence takes place:



Because of the high activation energy (30 kcal/mol) associated with this reaction<sup>20</sup> and the dependence of the reaction rate on temperature, quantity of radicals, etc., the anionic route is strongly favored. In general, free radical induced polymerization yields high molecular weight polymer.

## FILLERS AND ADDITIVES

Alkyl cyanoacrylate monomers typically have viscosities in the range of 1–3 cP, which are much too low to permit convenient use in many industrial applications. Water thin adhesives will flow from the bondlines, resulting in adhesive-starved joints and low bond strengths. Migrating adhesive could also bond adjacent

surfaces, as well as present possible safety hazards due to the adhesive's strong tissue bonding characteristics.

As a result, viscosity modification, through the use of various soluble *polymeric thickeners*, represented the first attempt to modify the liquid properties of cyanoacrylates. Thickeners and fillers must be compatible with the cyanoacrylates and must not set off the easily triggered anionic cure. Polymers which have been used to increase the base viscosity of the monomers include polymethacrylates (the most common), polyacrylates, polycyanoacrylates, polyvinylacetates, baked polyacrylics, polylactic acid, cellulose nitrates and other esters such

as the acetates, propionates and butyrates.<sup>3,22,23</sup>

Recently, *elastomeric fillers* have been incorporated into cyanoacrylates to improve the flexibility and toughness of the basically brittle polymers. Copolymers of: (a) acrylonitrile, butadiene, and styrene; (b) methacrylates, butadiene, and styrene; and (c) ethylene with methyl acrylate or vinyl acetate have been reported.<sup>24–26</sup> See the section on Recent Advances.

Earlier, ester *plasticizers* of various types were also reported to prevent the gradual embrittlement of the adhesive bond on aging. Those reported include cyanoacetates, succinates, adipates, sebacates, phthalates, acyl esters, phosphonates, and phosphates. Alkyl aryl

ethers have also been used.<sup>27,28</sup> Plasticized formulations with improved heat resistance were claimed by use of the allyl, methallyl, and crotyl esters of phthalic acid.<sup>29</sup> Further work to alleviate the brittleness of cyanoacrylate adhesives and to improve their impact, heat and moisture resistance, teaches the use of polyfunctional carboxylic acids and anhydrides.<sup>30,31</sup> Gallic acid, gallate esters, and tannin derivatives of gallic acid are reported to function similarly.<sup>32,33</sup>

Inorganic fillers are not widely used due to the likely instability which would be caused by these materials. Recently, stable *thixotropic gels* (see the section on Recent Advances) which can be applied to vertical or overhead surfaces have been prepared by Loctite. These materials are prepared from silane-treated hydrophobic silicas which are drier and considerably more stable than conventional silicas in cyanoacrylate adhesives.<sup>34</sup> The bond properties of these gels are identical to the flowable Newtonian cyanoacrylate adhesives.

Cyanoacrylates may be prepared in virtually any color. Stable dyes of assorted structures are used to color cyanoacrylates for cosmetic reasons or for inspectability during automated assembly operations.<sup>35-38</sup>

Considerable work has also been done in the last 10 years investigating the use of various additives which accelerate the anionic polymerization of cyanoacrylates on acidic or porous substrates. These additives are covered in the Recent Advances section of this chapter.

## PROPERTIES OF THE CURED ADHESIVES

The lower esters of the alkyl cyanoacrylates cure to clear, hard resins which exhibit good adhesion and tensile shear strengths to a wide variety of substrate combinations. They are, however, brittle and exhibit low peel and impact strengths. Higher viscosity versions of the lower esters filled with 5–10% of poly(methylmethacrylate) resins are somewhat less brittle and can offer double the impact strength of low viscosity monomeric adhesives, as well as significantly better peel strengths.

Property relationships amongst the simple

cyanoacrylate esters are shown in Table 2, and generally indicate that:

- Cure speed, tensile, tensile shear, and impact strength decrease with increasing ester chain length.
- Bond hot strengths also decrease with increasing alkyl chain length. In general, cyanoacrylates are not recommended for long term use above 60–70°C.
- Solvent resistance is typical of polar, linear high polymers. In nonpolar solvents, attack is negligible, while solvents of similar solubility parameter will weaken cured cyanoacrylate bonds slowly. (See Table 3). Moisture resistance of cyanoacrylates is not considered to be a strong point of these adhesives, however, with proper attention to adhesive and substrate composition, excellent bonds are achievable.

Several special esters also deserve mention, the allyl-2-cyanoacrylates and the  $\beta$ -alkoxy-alkyl cyanoacrylates.

Adhesives based on the *allyl ester* were first introduced by Eastman in the 1970s as thermally resistant products and have now been reintroduced by Permabond under the Powerbond trademark. These esters exhibit cure speeds and ultimate strengths similar to those of the ethyl and propyl products, but are capable of undergoing a second stage free radical crosslinking reaction through the pendant allyl group. The crosslinking reaction is sluggish, however, requiring significant exposures to high temperatures (350°F) to effect. The linear first-stage polymer will also soften considerably during this reaction, requiring that parts be supported in certain applications. Nonetheless, there are applications where the added thermal resistance of the allyl esters has proven essential.

The *alkoxy-alkyl esters*, which have methoxy or ethoxy groups appended to the  $\beta$ -carbon of a standard ethyl cyanoacrylate ester, are virtually odorless versions of cyanoacrylate adhesives. Though first reported by Eastman in 1957, these are now being reemphasized by several manufacturers with improvements in stability and cure speed. These will be covered more fully in the Recent Advances section.

Considerable work on *bis*-cyanoacrylates for

Table 2. Typical Properties of Common Cyanoacrylate Adhesives.

Monomer Type	Methyl	Ethyl	Isopropyl	Allyl	Bbutyl	Isobutyl	$\beta$ -Methoxy Ethyl CA	$\beta$ -Ethoxy Ethyl CA
<b>Bulk Properties</b>								
Softening point, °C (VICAT)	165	126	154	78	165	107	—	52
Melting point, °C	205	—	179	—	—	192	165	103
Refractive index, $n_D^{20}$	1.45	1.45	1.45	—	—	—	1.4	1.48
Dielectric const. @1 MH z <sup>a</sup>	3.34	3.98	3.8	3.3	5.4	—	—	—
Dissipation factor @1 MH z <sup>a</sup>	—	—	2.04	0.02	—	—	—	—
Volume resistivity, Megohms-mm	—	$3 \times 10^{15}$	$9 \times 10^{12}$	$7 \times 10^{14}$	$5.37 \times 10^9$	—	—	—
Tensile strength, steel/steel, psi	4500	4000	3000	—	—	2960	3550	4400
Elongation, %	<2	<2	<2	10	—	<2	—	—
Flexural modulus, psi	$4.93 \times 10^5$	$3.00 \times 10^5$	—	$2.54 \times 10^5$	—	—	—	—
Hardness (Rockwell)	M 65	M 58	R 18	—	—	—	—	—
All soluble in:	DMF, and CH <sub>3</sub> NO <sub>2</sub>							
Bond Properties	10-15	10-15	10-15	10-15	10	20	35	5
Set Times, seconds								
Steel/steel								
Al/Al	20	20	—	—	—	20	15	5
Nitrile rubber/nitrile rubber	5	5	—	—	—	5	5	3
ABS/ABS	20-30	10-15	—	—	—	20	5	3
Tensile Shear Strength, psi	3200	2500	3030	3120	2280	1420	2700	2400
Steel/steel								
Al/Al	2500	2000	1530	950	1013	1420	1650	1700
Impact shear, ft-lb/in. <sup>2</sup>	4-10	5-10	—	—	5.3	—	9-11	2.25

<sup>a</sup>ASTM D-150.<sup>b</sup>ASTM D-638.<sup>c</sup>ASTM D-790.<sup>d</sup>ASTM D-1002.<sup>e</sup>ASTM D950-54.

**Table 3. Solvent Resistance of Typical Methyl Cyanoacrylate Adhesive Bonds.<sup>48</sup>**

<i>Solvent at 24°C</i>	<i>Shear Strength<sup>a</sup> After 1-month Immersion, psi</i>
None (control)	2040
1,1,1-Trichloroethane	2540
Gasoline	2730
Acetone	26
Isopropyl alcohol	3000
10W-30 motor oil	2470
Naphtha	1640
Toluene	1680

<sup>a</sup>Steel-steel substrates.

improved thermal resistance has been done by first preparing the anthracene Diels-Alder adducts of monomers which were then reacted with glycols. The resultant intermediates were then reacted with excess maleic anhydride to generate the *bis*-monomer.<sup>39-44</sup> Improved thermal and solvent resistance were reported with these products, but the procedure is difficult and the final products very impure. The impurities undoubtedly prevent full realization of the benefits theoretically possible with these monomers.

Some work has also been done on copolymerizing cyanoacrylates with *bis*-cyanocarboalkoxy butadienes which claims significant improvements in thermal and solvent resistance.<sup>45</sup>

Some interesting and significant new work on cyanoacrylate adhesives with improved rheological, fast curing, and toughness properties will be covered in the section on Recent Advances.

## SUMMARY OF ADVANTAGES AND LIMITATIONS

Many of the advantages of cyanoacrylate adhesives have been previously discussed, and derive from their unique combination of attributes. Still a summary of these is in order. They include:

- *Ease of Use.* Cyanoacrylates are single-component adhesives that do not require mixing, clamping, external energy or long

times to cure. Most often a single drop, activated by adsorbed atmospheric moisture on parts held with finger pressure results in a bonded assembly within seconds. (See Table 3).

- *Speed of Cure.* Rapid polymerization occurs spontaneously within seconds to minutes. (See Table 4).
- *Strength and Versatility.* High strength bonds are achieved to a wide variety of metallic, plastic, and elastomeric substrates. (See Table 5).
- *Economy of Use.* Because of the minimal amount of adhesive required (1 drop/in.<sup>2</sup>) the cost of bonding is generally less than 1 penny per bond.

On the other hand, cyanoacrylate adhesives also have several well known limitations which restrict their use and preclude consideration as broad based general purpose adhesives. Elimination of these shortcomings has been the target of significant research and development by most manufacturers as the need to differentiate product lines intensifies.

## TYPICAL CYANOACRYLATE APPLICATIONS

The unique characteristics of cyanoacrylate adhesives virtually ensure their successful use over an extremely broad and diverse range of applications. The self-contained room temperature curing properties coupled with the ability to adhere to most surfaces combine to make cyanoacrylates the easiest way to assemble small, close fitting parts. So common are the uses of cyanoacrylate adhesives that each day it is a virtual certainty that each of us comes in contact with many items assembled using them.

In the automotive market, cyanoacrylates are used to bond weatherstripping to automotive bodies and to position rubber gaskets before assembly. They are used to bond polycarbonate positioning clips to side windows of automobiles, alternator horn assembly components, and rubber gaskets to automotive thermostats. One of the most common automotive applications is the use of cyanoacrylates in the repair of flexible PVC side trim strips.

Cyanoacrylates are ideal for bonding small

**Table 4. Effect of Adherend Combination on Bonding Action and Strength.<sup>57</sup>**

<i>Substrate</i>	<i>Bonding Action</i>	<i>Bond Strength</i>
Glass-glass	rapid	strong initial
Aluminum-aluminum	intermediate	intermediate
Steel-steel	intermediate	strong
Glass-rubber	rapid	strong
Porcelain-porcelain	rapid	strong
Polyethylene-polyethylene	intermediate	intermediate
Polyester-polyester	rapid	intermediate
Tenite® acetate-		
Tenite® acetate	intermediate	strong
Tenite® butyrate-		
Tenite® butyrate	intermediate	strong
Metal-cork	rapid	strong
Metal-felt	rapid	strong
Glass-cork	rapid	strong
Glass-felt	rapid	strong
Wood-wood (maple)	slow	strong
Metal-leather	intermediate	strong
Metal-rubber	rapid	strong
Rubber-rubber	rapid	strong
Rubber-cardboard	rapid	strong
Glass-steel	intermediate	strong
Nylon-nylon	rapid	intermediate
Glass-Tenite® butyrate	intermediate	intermediate
Steel-Neoprene	rapid	strong

**Table 5. Shear Strengths of Bonds Formed by Methyl Cyanoacrylate Adhesives.<sup>57</sup>**

<i>Substrates</i>	<i>Shear Strength of Adhesive Bonds, psi</i>	
	<i>Age of Bond</i>	<i>Eastman 910® Adhesive</i>
Steel-steel	10 min	1920
	48 hr	3000
Aluminum-aluminum	10 min	1480
	48 hr	2700
Butyl rubber-butyl rubber	10 min	150 <sup>a</sup>
SBR rubber-SBR rubber	10 min	130
Neoprene rubber-neoprene rubber	10 min	100 <sup>a</sup>
SBR rubber-phenolic	10 min	110 <sup>a</sup>
Phenolic plastic-phenolic plastic	10 min	750
	48 hr	—
Phenolic plastic-aluminum	10 min	650
	48 hr	920
Aluminum-nylon	10 min	500
	48 hr	1440
Nylon-nylon	10 min	330
	48 hr	1400
Neoprene rubber-glass filled polyester	10 min	110 <sup>a</sup>
Acrylic plastic-acrylic plastic	10 min	810 <sup>a</sup>
	48 hr	790 <sup>a</sup>
ABS-ABS	10 min	640 <sup>a</sup>
	48 hr	710 <sup>a</sup>
Polystyrene-polystyrene	10 min	330

<sup>a</sup>Substrate failure.



electronic components such as phonograph needle cartridges and for tamperproofing video cassettes. Electrical coil wires are terminated and transformer laminations unitized with cyanoacrylate adhesives. Printed circuits are modified with adhesive tacked wire connections and the boards themselves often repaired with cyanoacrylates. Audio high fidelity speakers are using increasing amounts of cyanoacrylates in preference to two-component, heat cured epoxies.

Cosmetic items such as lipstick tubes, mirrors in compacts and eyeshadow containers, brush tips and applicator swabs are also assembled with cyanoacrylates.

Sporting goods and toys are also important application areas. Items such as athletic shoes, swim masks, trophies, rubber foam recoil pads for shotguns, as well as the feather fletches on an archer's arrows, all benefit from cyanoacrylates' unique bonding capabilities. Rubber dolls and plastic doll house furniture are but two of the many toys that utilize cyanoacrylates in manufacturing.

Many medical and dental devices are now being assembled with cyanoacrylates to eliminate costly molding procedures. Cyanoacrylates are also being employed to eliminate the toxic solvents commonly used to bond flexibilized PVC in tubing joints.

Though not approved in the United States for surgical use, cyanoacrylates' strong tissue bonding capabilities have resulted in their use as chemical sutures and hemostatic agents in many foreign countries. Many lives were saved in Viet Nam through the use of Eastman Kodak developed cyanoacrylate spray kits which enabled battlefield medics to stop massive blood loss, a prime cause of combat death.

With the incorporation of the new surface-insensitive additives which allow rapid curing on acidic and porous substrates such as wood and paper, and the marketing of these versatile adhesives in the consumer sector, the number of applications where cyanoacrylates are used is limited only by the ingenuity of the user. The new toughened adhesives with improved heat and humidity resistance and dynamic performance are already encroaching into areas where epoxies were once the only choice. Versatility

will be a key factor in the continuing growth of cyanoacrylate adhesive applications.

## REQUIREMENTS FOR SUCCESSFUL USAGE

In order to bond materials utilizing cyanoacrylates, it is necessary to remember that polymer formation initiates at the adhesive-substrate interface when the adhesive comes in contact with the surface layer of moisture present on the substrate. Polymerization then proceeds back toward the center of the adhesive layer rather than uniformly throughout the mass. As a result, cyanoacrylate adhesives are not efficient gap filling adhesives, since as the gap increases the likelihood of a growing chain being terminated by an inhibitor molecule becomes quite high.

As with all adhesives, substrate cleanliness is the key to strong, durable bonds. It is essential that all mold releases, oils, residual acids, etc., be removed initially. This can best be accomplished by wiping the surface with a cloth wetted with acetone or naphtha. If the surface itself is acidic, a wash in a mildly alkaline solution or treatment with a cleaning-activator solution is recommended. For metal bonding, the surface should be solvent cleaned, abraded with sandpaper, followed again by a solvent wash.

Once the surfaces are properly prepared, care should be taken to ensure the use of only the minimum amount of adhesive (one drop per in.<sup>2</sup> is recommended) needed to fill the bondline. Excess adhesive can result in slow cures.

For rapid fixture times, the adhesive used should be as fresh as possible. Old adhesive tends to be slower, as acidic stabilizers gradually hydrolyze the monomer, forming carboxylic acids. To maintain the quality of the adhesive, bottles should be kept tightly closed and stored in a cool, dark location. Cyanoacrylates can be safely stored in most polyethylene, polypropylene, and aluminum containers.

## TOXICITY

There is currently a lack of significant data on the toxicity characteristics of cyanoacrylate monomers—this is mainly because the mon-

omer polymerizes so rapidly that most standard tests (such as inhalation toxicity, etc.) are precluded.

The work of McGee et al.<sup>46</sup> shows that cyanoacrylate vapors can be irritating to the nose and throat at levels as low as 3 ppm; eye irritation was also experienced at levels of approximately 5 ppm and greater. Because the material has yet to be completely evaluated, prolonged breathing of cyanoacrylate vapors should be avoided. Only methyl cyanoacrylate has a listed TLV (2 ppm) and short-term exposure limit (4 ppm).<sup>47</sup> Workers exposed to these materials should be provided with adequate ventilation. (TLV is "Threshold Limit Value" for continuous exposure, per American Conference of Governmental Industrial Hygienists.)

Studies carried out on *polymerized* cyanoacrylates revealed that oral doses of 6400 mg/kg failed to kill laboratory rats.<sup>48</sup> While the adhesive did cause mild irritation of the skin of guinea pigs after 24 hours exposure, there was no evidence of skin sensitization or absorption through the skin.

Cyanoacrylates are considered combustible liquids. The monomer and cured adhesive will both support combustion. As a result, all work with cyanoacrylates should be done away from areas of open flame, sparks, and high heat.

Obviously, contact with skin should be avoided; not only is the material a powerful adhesive, but when polymerization does occur, a rapid exotherm is evolved.

## RECENT ADVANCES

As previously discussed, conventional cyanoacrylates perform well in numerous bonding applications, but several well known and significant limitations preclude even wider usage. It is toward these limitations that much recent research and development work has been directed. These limitations, partially reviewed in previous sections, include:

- Lack of true engineering adhesive performance:
  - Poor impact/peel properties
  - Low thermal resistance
  - Attack by some solvents

Embrittlement on heat exposure

Poor thermal/humidity cycle resistance

- Sensitivity of cure on porous and acidic surfaces
- Low gap filling ability
- Liquid migration
- Lachrymatory irritating odor
- Fogging of adjacent bright or transparent surfaces

Significant progress in addressing and resolving these performance shortfalls has been made over the last several years.

## Toughened Adhesives

The ultimate quality of the cyanoacrylate adhesive bond falls short of what is normally considered desirable for a true engineering adhesive, in terms of long term durability and thermal, moisture, and solvent resistance. This is due in part to the thermoplastic nature of the polymer, and the relatively high shrinkage of the lightly filled adhesives. It is also generally accepted that the bonds have a higher than average susceptibility to attack by moisture, although it has been shown in early Eastman literature<sup>48</sup> and by O'Connor and Zimmermann<sup>49</sup> that weather resistant, long lived cyanoacrylate bonds between metals and elastomeric materials are achievable.

Various workers in the late 1970s began to look at different methods of reducing the brittleness of cyanoacrylate bonds, through the use of rubber toughening agents or other impact improving additives. ABS, MBS, MABS,<sup>24,25</sup> and acrylic polymers<sup>26</sup> have been shown to be advantageous in improving the peel, impact, and thermal resistance of cyanoacrylates. Several other acidic impact-improving or adhesion-promoting additives have also been reported to lessen the brittleness and improve the thermal resistance<sup>30,31,33</sup> of cyanoacrylate adhesive bonds. The improvements that toughened adhesives exhibit are quite substantial (Table 6), particularly after heat aging. Conventional adhesives lose a significant portion of their properties after short heat aging, while toughened adhesives show much better property retention. Similar improvements are seen in temperature/humidity cycling tests (Table 7),

**Table 6. Bond Embrittlement on Heat Aging.<sup>a</sup>**

<i>Adhesive</i>	<i>Tensile Shear Strength, psi</i>			<i>Impact Strength, ft-lb/in.<sup>2</sup></i>		
	<i>5 Days RT</i>	<i>Heat Aged, 2 hr, 250°F</i>	<i>Heat Aged, 24 hr, 250°F</i>	<i>5 Days RT</i>	<i>Heat Aged, 2 hr, 250°F</i>	<i>Heat Aged, 24 hr, 250°F</i>
High Visc. Ethyl	3020	2750	1410	8.5	9.6	2.0
High Impact "A"	2930	1700	360	7.8	1.4	1.0
High Impact "B"	3080	1730	1330	10.2	5.7	2.2
BLACK MAX™	3090	3770	3920	10.2	13.7	9.1
Rubber Toughened						

*Specimens:* Sandblasted steel lap shear strips.

"A" and "B": commercially available cyanoacrylates.

<sup>a</sup>Testing carried out at room temperature.

**Table 7. Cyclic Heat/Humidity Resistance on Abraded Aluminum**

	<i>5 Day RT</i>	<i>25 Cycles</i>	<i>50 Cycles</i>
Pacer TX100 <sup>a</sup>	733	250	6
Pacer MR150 <sup>a</sup>	1827	Fail	Fail
Henkel 8400 <sup>b</sup>	933	375	213
Loctite Tak Pak™ <sup>c</sup>	1273	260	210
Loctite 498-TCR™ <sup>c</sup>	1987	860	543
Loctite Black Max™ <sup>c</sup>	2410	2130	1865

*Specimens:* As-received aluminum lapshear prepared with 3M Scotch-Brite pads with reagent-grade acetone wash.

*Cycle Conditions,* (3 hr cycle):

30 min @ -20°F

1 hr ramp to 150°F

30 min @ 150°F, 95% RH

1 hr ramp to -20°F

\*TCR—Thermal Cycle Resistant

*Suppliers:*

<sup>a</sup>Pacer Technology, 1600 Dell Ave., Campbell, CA 95008

<sup>b</sup>Henkel Adhesives Co., div. Henkel Corp., 4620 West 77th St., Minneapolis, MN 55435

<sup>c</sup>Loctite Corp., 705 North Mountain Rd. Newington, CT 06111

which strongly suggests that temperature cycling plays a strong role in the reported low humidity resistance of cyanoacrylate adhesives. A plausible explanation for this behavior would be that the lightly filled conventional cyanoacrylate adhesives do not cure fully at room temperature, but do postcure during heat aging, with resultant shrinkage. As the adhesives are surface activated, the stress is concentrated at the bond line since the monolayer at the interface is the first to cure. The function of the rubbers and toughening additives may be to relieve these stresses. Surprisingly, in some cases, this results in improved bond hot strengths despite the fact that polymer thermal stability remains unchanged.

## Thermal Resistance

Long term thermal resistance of cyanoacrylate adhesives where constant exposure to temperatures greater than 60–80°C is required remains a problem. As already mentioned, an early approach was to substitute an allyl group in the side chain in place of the saturated alkyl group.

Increased thermal resistance was claimed via a two-stage cure mechanism, whereby thermally induced crosslinking occurs after anionic polymerization of the cyanoacrylate double bond. In practice, however, the crosslinking is very slow, and assembled parts might have to be supported until it takes place.<sup>50,51</sup>

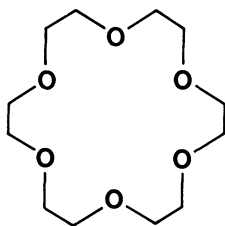
Anhydrides of polyfunctional carboxylic acids, as well as the acids themselves, have been reported to improve the thermal resistance as well as impact toughness of cyanoacrylate adhesives.<sup>30,31</sup> Bond hot strengths are improved substantially, even though the thermal decomposition temperatures of the polymer remain unchanged.

### Improved Curing Characteristics

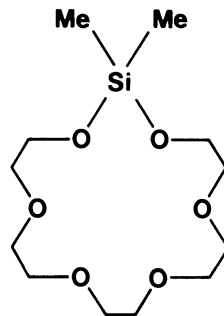
The sensitivity of the cure of cyanoacrylates to various substrates, notably acidic surfaces which inhibit or slow the anionic cure, has also been a recurrent problem. This had been overcome by the use of various basic surface acti-

vators marketed by most cyanoacrylate manufacturers, but in fast production environments the use of a second component in the assembly process is often undesirable. Recent patents have been filed or issued teaching the use of crown ethers,<sup>52</sup> silacrowns,<sup>53</sup> calixarenes,<sup>54</sup> and various linear polyalkylene ethers<sup>55,56</sup> as curing additives for use on wood and porous surfaces (see Fig. 1). These additives are remarkably effective in accelerating cures on such substrates and even seem to be effective in promoting the cure of cyanoacrylate adhesives under conditions of low relative humidity. The slowing of cure rates during the low humidity winter months can cause severe problems on fast automated assembly lines. The

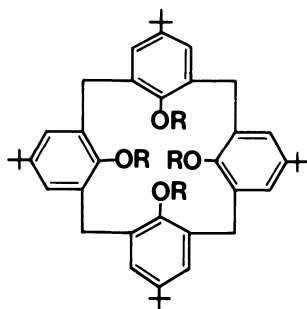
18-CROWN-6



1, 4, 7, 10, 13, 16-HEXA-OXA-CYCLOOCTADECANE



1,1 DIMETHYLSILA 17-CROWN-6



5, 11, 17, 23, TETRA-t-BUTYL  
25, 26, 27, 28 TETRA (2-ETHOXY-20XO)  
ETHOXY-CALIX-4-ARENE

Fig. 1. Curing additives for lessened surface sensitivity.

mechanisms of action for these additives is not fully understood, but since the crown compounds are phase transfer catalysts some interaction with alkali metals in the surface seems likely.

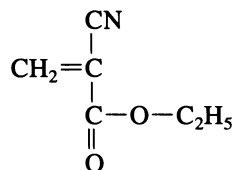
### Thixotropic Gels

Highly thixotropic gel versions of cyanoacrylates have also become available, thickened with a combination of the normal poly(methyl methacrylate) resins and various hydrophobic fumed silicas.<sup>34</sup> Unmodified silicas generally yield very unstable products due, at least in part, to the large amounts of absorbed water. The new products are very easy to apply even on parts with three-dimensional bondline configurations and will not run off of vertical surfaces. Migration from the bondline is totally eliminated, preventing any undesirable movement into other critical areas. User safety with these new gels is greatly enhanced since the possibilities of splashing or running onto exposed skin are considerably reduced. Recently introduced into the consumer market as a more user friendly instant super glue, the gel is finding wide acceptance. Surface insensitive versions with improved curing characteristics are now being introduced which will move the cyanoacrylates towards a more universal adhesive market segment.

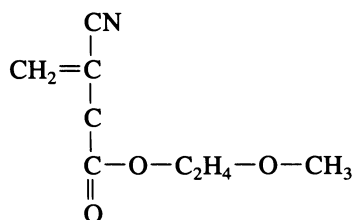
### Low Odor—Low Bloom Cyanoacrylates

Anyone who has used cyanoacrylates on a continuous basis in an area with poor ventilation is familiar with the pungent, irritating, acrylic-type odor. The relatively high vapor pressure of the cyanoacrylate monomers which contributes to the odor can also cause evaporation from uncured fillets; the vapors precipitate as a white haze on surfaces adjacent to the bondline. On bright, decorative, or transparent parts this may be unacceptable, often requiring the use of an alternative adhesive. Good ventilation helps, but not universally. This has led to the development and marketing of alkoxyalkyl cyanoacrylate adhesives, which structurally are merely ethyl cyanoacrylates with methoxy or ethoxy

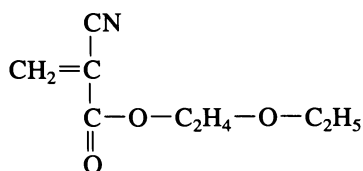
groups attached to the  $\beta$ -carbon of the ester side chain:



standard ethyl cyanoacrylate



methoxyethyl cyanoacrylate



ethoxyethyl cyanoacrylate

These monomers are virtually odorless and have much lower vapor pressures so that the blooming characteristics are greatly reduced or eliminated. Performance is similar but not equivalent to that of the lower methyl and ethyl esters. On metals or rubber the cure speeds are quite fast, but the cure speeds on plastics were slower than conventional cyanoacrylates. Updated, faster curing versions of these products are becoming available. As costs of production for these adhesives are reduced, and the curing properties improved, they are expected to replace the lower esters in many applications.

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# Polyester and Polyamide High Performance Hot Melt Adhesives

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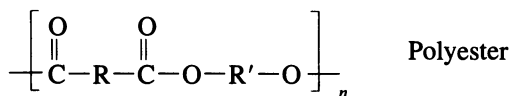
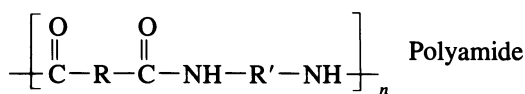
Hot melt adhesives have been known for centuries. Historically, mixtures of natural waxes, rosin, pitch, and other naturally occurring substances were used alone or in mixtures to produce sealing compounds for a variety of applications. It was not, however, until the early 1950s that hot melts based on synthetic polymers appeared in the marketplace.

Traditionally, as now, hot melts usually have been made by compounding existing high molecular weight polymers with low molecular weight resins to achieve the desired balance of properties. A great diversity of hot melts is now available from synthetic resins and polymers based on petroleum feed stock. Of all these, it is the compounded polyamides and polyesters which provide hot melts with the best properties.

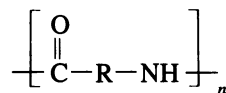
The chemistry for these two classes of polymers goes back to the pioneering work of Wallace Carothers at DuPont which led to the development of nylon 6-6, poly(hexamethylene adipamide), the first man-made fiber. Carothers also investigated the aliphatic polyesters, but found them too low in melting point to serve as fibers. In England, however, J. R. Whinfield and J. T. Dickson of Calico Printers Association [British Patent 578,079 (1946)] developed

polyesters from aromatic dibasic acids, including polyethylene terephthalate (PET), now the major synthetic polymer for fibers.

Most polyamides and polyesters are condensation polymers, produced by reacting dibasic acids with diamines to produce polyamides, or with diols to make polyesters. If derived from dibasic acids, the chemical structures can be represented as follows:



If produced by ring opening of caprolactam or other lactam, the polyamide structure is:



In homologous series of polyesters and polyamides, the melt points,  $T_m$ , of polyesters are significantly lower than those of polyamides. As the proportion of carbon atoms in the main chain is increased, the melt points of polyam-

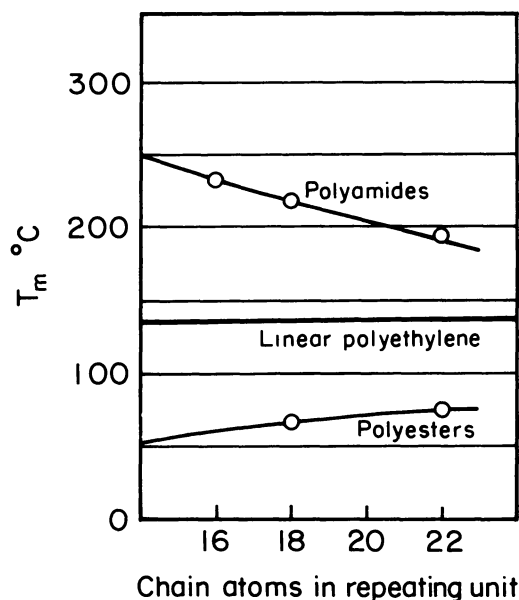


Fig. 1.

ides decrease while those of polyesters increase, both approaching the melt point of polyethylene as shown in Fig. 1.

The low melt points of polyesters are associated with the flexibility of the C—O chain bond and the low heat of fusion. The substantially higher melting point of the polyamides are the result of intermolecular hydrogen bonding across amide groups of adjacent molecules.

The melt point is also affected by the spacing of the polyester and amide groups since this determines the crystal structure of these polymers. The even-number carbon chains have higher crystallinity and therefore higher melt points. This trend is shown in Fig. 2 for polyesters made from decamethylene glycol and dibasic acids of varying chain lengths and for polyamides made from sebacic acid and diamines of varying chain length.

## POLYAMIDES

Because the polyamides and the polyesters developed for fibers are too high-melting and too fast-setting to be used for adhesives, chemists have made copolymers to lower the melt point and increase the set time of these two classes of polymers. Today most of the polyamides and polyesters used in hot melt adhesives are based either on monomers not used for fibers or, more

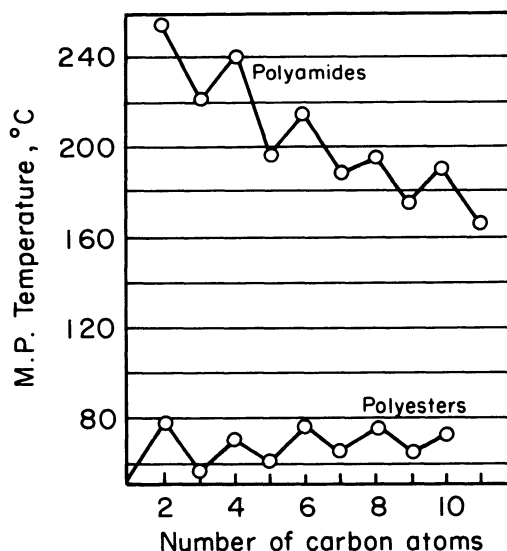


Fig. 2.

commonly, on copolymers. The most common monomers for hot melt polyamides are:

- *Dibasic Acids:*  
Dimer acid (dimerized fatty acids).  
Dodecanedioic acid.  
Sebacic acid.  
Azelaic acid.  
Adipic acid.
- *Amino Acids and Lactams:*  
Caprolactam.  
11-Aminoundecanoic acid.  
Dodecalactam.
- *Diamines:*  
Ethylene diamine.  
Hexamethylene diamine.  
Diethylene triamine.  
Triethylene tetramine.  
Piperazine.  
Dipiperidyl propane (Dipip).  
Polyoxypropylene diamine.

From these monomers have been developed a large variety of polyamides, which can be divided into four classes:

1. Polyamides made from lactams and amino acids.
2. Polyamides from condensation reactions of short chain dibasic acid and diamines.
3. Polyamides from long chain, vegetable oil-derived dibasic acids and short chain diamines.

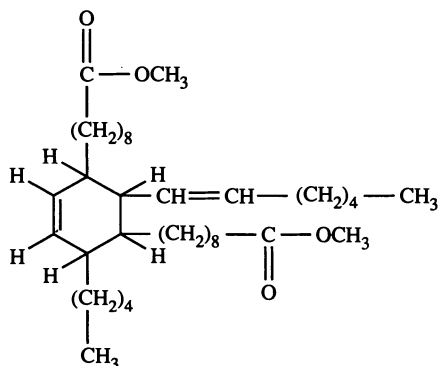


#### 4. Polyamide copolymers and terpolymers of short chain monomers.

The homopolymers of the first two classes represent all the nylon fibers, as well as all the engineering nylon plastics.

To the third class belongs most of the low melt high melt polyamides.

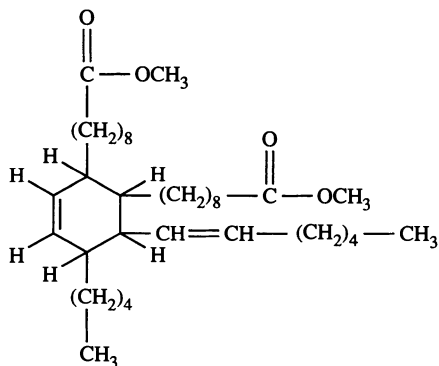
The fourth class includes a very large group of polyamides derived from a multiplicity of monomers, resulting in very specialized hot melt adhesives.



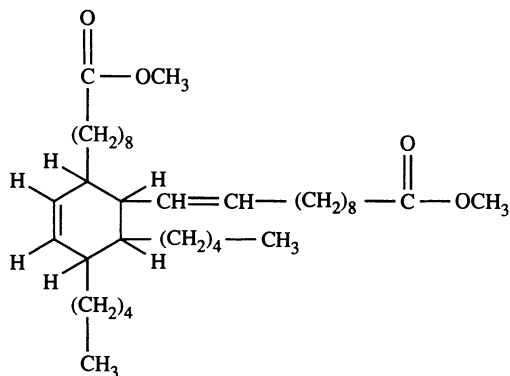
2A

#### Dimer Acid-Based Polyamides

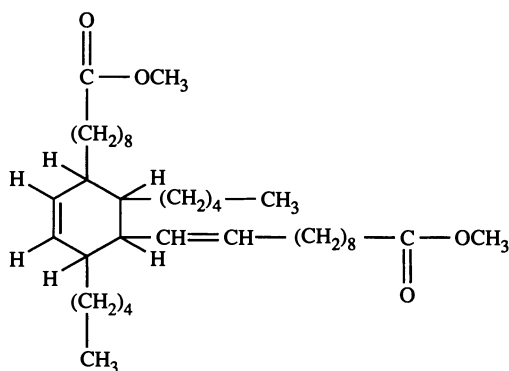
The dimerization of  $C_{18}$  unsaturated fatty acids produces mainly dibasic acids with carbon chain lengths of 36 carbon atoms. Wheeler<sup>2</sup> has suggested several alternate  $C_{36}$  diacid structures that may be present, along with  $C_{18}$  and  $C_{54}$  acids, in commercial dimer acid (methyl ester):



1A



1B



2B

The mixture is subjected to molecular distillation to obtain dimer acids of higher purity.

The reaction of dimer acids with short chain diamines such as ethylene diamine results in amorphous polyamides with sharp melting points which set rapidly. This was discovered by scientists at the Northern Regional Laboratory of the United States Department of Agriculture.<sup>3</sup> It was soon observed that these diamines would react with liquid epoxy resins in substantially stoichiometric ratios to yield crosslinked networks.<sup>4</sup> By reducing the amount of epoxy resin significantly below stoichiometric proportions, it was possible to obtain thermoplastic adhesives that function as hot melts.<sup>5</sup>

The first commercial dimer acid polyamides were produced by General Mills under the trade name "Versamid," and are now available from Henkel. The properties of these resins are summarized in Table 1.

Shortly thereafter, Emery Industries, the first commercial producer of dimer acid, entered the thermoplastic polyamide market with similar

**Table 1. Henkel Resins.**

<i>Versamid Reactive Resins</i>				
<i>Properties</i>	<i>100</i>	<i>115</i>	<i>125</i>	<i>140</i>
Amine value	83-93	210-220	290-320	350-400
Softening point, °C.	43-53	viscous fluid	fluid	fluid
ASTM E-28, Modified				
Flash point, °C,	325	295	265	185
ASTM D-92				
Ash, % by weight	0.05	0.05	0.05	0.05
Specific gravity, 25°C/25°C	0.98	0.99	0.97	0.97
Pounds/gallon, 25°C	8.2	8.3	8.1	8.1
Color, Gardner	12 max.	12 max.	12 max.	12 max.
Viscosity, cps:				
25°C	—	—	45,000-55,000	12,500-17,500
40°C	—	50,000-75,000	8000-12,000	3000-6000
75°C	—	3100-3800	700-900	200-600
150°C	700-1200	—	—	—
<i>Versamid Thermoplastic Resins</i>				
<i>Properties</i>	<i>900</i>	<i>930</i>	<i>940</i>	<i>950</i>
Amine value	3-8	3-8	3-8	3-8
Softening point, °C,	180-190	105-115	105-115	90-100
ASTM E-28 <sup>a</sup>				
Penetration, 25°C,	2	3	4	15
ASTM D-5, Modified				
Flash point, °C,	350	339	332	291
ASTM D-92				
Ash, % by weight	0.05	0.05	0.05	0.05
Specific gravity, 25°C/25°C	0.98	0.98	0.98	0.98
Pounds/gallon, 25°C	8.2	8.2	8.2	8.2
Color, Gardner, solid	12 max.	12 max.	12 max.	12 max.
Viscosity, cps:				
150°C	—	3000-4500	1500-3000	700-1500
200°C	300-400	—	—	—

<sup>a</sup>Ring and ball method.

resins trade named "Emerez," as shown in Table 2.

These solid polyamides for hot melts were made by reacting dimer acid with ethylene diamine. Reactive resins, designed as curing

agents for epoxies, were made by reaction of dimer acid with a stoichiometric excess of diethylene triamine or triethylene tetramine.

The reaction of dimer acid with ethylene diamine produced resins with softening point

**Table 2. Emery Industries Emerez Resins.**

	<i>1530</i>	<i>1540</i>	<i>1532</i>	<i>1535</i>
Amine value, mg KOH/gm,				
ASTM D-1980-61	4	4	4	4
Acid Value, mg KOH/gm,				
ASTM-D-2074=62T	4	4	4	4
Softening point, °C,				
ASTM E-28	105-115	105-115	105-115	127-135
Ash, % by weight	0.05	0.05	0.05	0.05
Specific gravity, 25°C/25°C	0.98	0.98	0.98	0.98
Pounds/gallon, 25°C	8.2	8.2	8.2	8.2
Color, Gardner	12 max.	12 max.	12 max.	12 max.
Viscosity, cps, 160°C	2100-2700	1200-1800	2800-3300	500-1000

around 105–110°C. Substitutions of shorter dibasic acid, such as adipic, azelaic or sebacic, for a portion of the dimer acid resulted in an increase of 5–25°C in softening temperature.

These resins were somewhat brittle. They bonded well to porous substrates but found limited application unless modified by compounding in order to improve flexibility and adhesion to nonporous surfaces. For example, blending of solid thermoplastic resins with the reactive polyamides resulted in hot melt adhesives which bonded well to metals and other substrates, and also had improved flexibility.

Properties would also be modified by compounding with tackifying resins, plasticizers, etc., among them the following (asterisks denote the most popular modifiers):

Tackifying Resins	Plasticizers
* Rosin	* Paratoluene sulfonamide
* Dimerized rosin	
* Rosin esters	* N-Ethyl paratoluene sulfonamide
Rosin phenolics	
* Ketone resins	N-Cyclohexyl paratoluene sulfonamide
Modified phenolic resins	Triphenyl phosphate
Maleic resins	Tributyl phosphate
	Phthalate esters
	Castor oil

The first polyamides were relatively low in molecular weight and required considerable compounding to produce good adhesives. However, as the purity of dimer acid improved, higher performance polyamides with higher melt points, greater strength, and better adhesion became available from General Mills

(now Henkel) under the trade name "Versalon" (Table 3).

Versalon 1140 represents a family of polyamides with unique adhesion characteristics. It was one of the first polyamides with a wide range of adhesion including fair to good adhesion to vinyl. The polyamides are believed to be based on secondary heterocyclic diamines, as disclosed in U.S. Patent 3,377,305.<sup>5</sup>

Later, another supplier of dimer acid, Union Camp, introduced a variety of dimer acid-based polyamides under the trade name "Uni-Rez" (Table 4).

In addition to the sources mentioned, special hot melt polyamides derived from dimer acid are available from Bostik Division of Emhart Corp., Terrell Industries, and Dexter Hysol. Some of these polymers are listed in Tables 5 and 6.

Most polyamide adhesives are characterized by

- Sharp melt point
- Excellent adhesion to a wide variety of substrates, including treated polyethylene and polypropylene
- Excellent color and low odor
- Good moisture vapor barrier properties
- Good chemical and oil resistance
- Resistance to blocking

Most polyamides, and particularly the dimer acid polyamides, are prone to oxidation and must be stabilized by antioxidants, or by blanketing the surface of the melt with dry nitrogen. Polyamides made from hydrogenated dimer acid are considerably more stable to oxidation, but at substantially higher cost.

The stabilizers vary with the polyamide. Generally, a blend of antioxidants is used; the most common of these are hindered phenolics,

**Table 3. Henkel Versalon Resins.**

Property	1112	1165	1175	1140
Softening point, °C, ASTM E28	112	165	172	140
Specific gravity	0.95	0.98	0.95	—
Viscosity, cps:				
190°C	3,700	4,000	8,000	—
225°C	1,600	1,500	2,200	8,500
Tensile strength, psi, 23°C	2,000	850	2,100	700
Elongation, %, 23°C	300	600	450	900

**Table 4. Union Camp Uni-Rez Adhesive Grade Polyamides.**

<i>Property</i>	<i>2651</i>	<i>2622</i>	<i>2643</i>	<i>2641</i>	<i>2624</i>	<i>2665</i>
Melting point, °C	100	107	124	138	162	165
Viscosity, cps, 190°C	9000	900	2000	8500	7500	8500
Color, 40% in <i>n</i> -butanol	5	6	5	4	6	5
Pounds/gallon at 25°C	8.0	8.2	8.1	8.2	8.1	8.1
Tensile strength, psi	550	1400	400	700	1400	2000
Elongation, %	900	50	250	700	500	500
Tensile modulus, psi	12,000	36,000	9,000	7,000	25,000	55,000
Tensile impact, ft.-lb/in. <sup>2</sup>	160	5	120	150	50	70
Low Temperature impact brittleness, % passed at -20°C	100	—	—	—	—	—

phosphites, phosphates, phosphoric acid, and hindered aromatic amines.

These adhesives are available in several forms: pellets, monofilament, ground resins, billets, and glue sticks. The pellets and ground resins can be applied with standard bulk hot melt applicators. The monofilaments, first developed by Bostik, are applied with specialized melting equipment. The billets are applied with modified bulk melt equipment which melts only the surface of the billet in contact with a heated

grid. Glue sticks are applied with a glue gun, a hand held melt device.

Hot melt applicators for melting polyamides are available from several suppliers, notably, Nordson, Meltex Corp., Bostik Fastening Systems Group, and Graco/LTI.

#### Adhesion vs. Composition

The various polyamides have a broad range of adhesive properties. They bond well to porous

**Table 5. Bostik Hot Melt Polyamide Adhesives.**

<i>Property</i>	<i>4254</i>	<i>4252</i>	<i>7279</i>	<i>7228</i>
Softening Point, ASTM E-28	112	132	163	182
Melt viscosity, cps				
149°C	5,300	—	—	—
177°C	—	5,600	—	—
204°C	2,300	2,200	7,000	7,000
Tensile at break, psi	1,100	2,100	1,500	1,400
Elongation at break, %	75	200	100	60

**Table 6. Terrell Terlan Polyamide Adhesives.**

	<i>230</i>	<i>652</i>	<i>685</i>	<i>1560</i>	<i>1583</i>
Softening point, ball and ring, °C	110	174	191	139	160
Melt viscosity, cps					
149°C	5,000	—	—	—	—
191°C	—	9,500	—	—	—
204°C	—	—	—	3,500	—
210°C	—	—	—	—	12,000
232°C	—	—	8,500	—	—
Tensile at break, psi	1,200	2,200	2,000	400	2,200
Elongation at break, psi	50	100	100	1,200	400

substrates and polar surfaces. However, the faster setting types do not bond well to metal unless the metal is preheated to allow better wetting.

Most of the general type polyamides do not bond well to vinyl. Slower setting polyamides, synthesized by reacting dipiperidyl propane, have improved adhesion to vinyl and cold metal. These polyamides are lower, however, in heat resistance and resistance to oil and solvents.

### Application Systems

Bostik Division of Emhart Corporation pioneered the use of polyamide hot melt for bonding leather in shoe manufacturing. In 1953 this company commercialized a process using hot melt polyamides in monofilament form. This composition, with a melt point of about 105°C, made by properly compounding commercially available polyamides, was passed through a specially designed melt body which melted a small amount of adhesive at any given time. This patented process<sup>6</sup> was used for folding shoe upper leather prior to the stitching operation.

At a later date, the same company developed<sup>7</sup> a process for hot printing a polyamide supplied in filament form to the toe portion of shoe up-

polyamides. For example, high melting polyamides with melt point above 160°C are used in bonding paper for oil filters. In this application, polyamides capable of withstanding 149°C are being used.

Polyamides designed for bonding plastics are functioning to make heat-shrinkable sleeves in electrical applications and for sealing electrical connectors. Polyamides containing a secondary diamine, with a wide softening range, are chosen because of their better adhesion properties and easy activation.

Specially designed polyamides with high melt points, but very low modulus, serve to encapsulate electrical connectors. This type of polyamide is also being foamed with a Nordson Foam Melter for a gasket in microwave ovens.

### Nylon-Type Polyamide Hot Melts

When lactams are homopolymerized or short chain dibasic acids are reacted with diamines, high melt point polyamides suitable for fibers or engineering plastics are obtained. Nylons derived from lactam or amino acids are designated by the number of carbon atoms in the amino acids, while the nylons derived from the reaction of dibasic acids and diamines are given two numbers, the number of carbon atoms in the diamine and dibasic acid respectively:

Monomer	Nylon No.	Melt Point, °C
Caprolactam	Nylon 6	225
Lauryl lactam	Nylon 12	180
1,1-Aminoundecanoic acid	Nylon 11	185
Adipic acid + hexamethylene diamine	Nylon 6-6	264
Azelaic acid + hexamethylene diamine	Nylon 6-9	210
Sebacic acid + hexamethylene diamine	Nylon 6-10	222
Dodecanedioic acid + hexamethylene diamine	Nylon 6-12	212

pers. The leather, with the printed hot melt, was then softened in presence of steam and lasted on a shoe last. On cooling, a firm box is obtained. The property of this polyamide to be softened by the presence of steam allowed the softened upper to be lasted easily. Polyamides also function in other shoe bonding operations, such as side lasting, toe lasting, and heel seat lasting.

Other applications of polyamides take advantage of the good oil resistance of the higher melt

These polymers are too high melting and too high in viscosity to be suitable for hot melts, except for a very few specialized applications. However, copolymers and terpolymers of the above monomers are suitable for hot melts, since the disruption of regularity in the polymer chain reduces the crystallinity and the formation of hydrogen bonds between the amide groups, resulting in lower melting points and more flexible products.

Reduction of hydrogen bonding and there-

fore lower melt points can also be achieved by condensing a secondary diamine, as the resultant  $-\text{CO}-\text{NR}-$  groups are incapable of hydrogen bonding with adjacent molecules. Thus the N-methylation of 50% of the amide groups in Nylon 6,6 results in a  $120^{\circ}\text{C}$  lowering of softening point.

Polymerization of three or more monomers results in further disruption of hydrogen bonding with the consequent reduction in melt point and chemical resistance of the polymers obtained.

Many terpolymers have been synthesized and are commercially available. This class of polyamide constitutes the basis of many of the hot melt, nylon type polyamides, which are used extensively in fabric bonding.

Example of the terpolymers available are:

Terpolymer	Producers
Nylon 6, 6-6, 6-10	DuPont
Nylon 6, 6-6, 12	Emser Werke, Huels, Rilsan (div. ATO Chemie)
Nylon 6, 6-6, 6-12	Bostik
Nylon 6, 6-9, 6-12	Bostik

The composition of these polymers can be plotted on three-component diagrams which show the area of compositions with desirable melt points for adhesives. Examples of such compositions taken from U.S. Patent 3,919,033<sup>8</sup> are shown in Fig. 3.<sup>6</sup>

Many of these hot melt adhesives are used in fabric bonding. They are softened by steam, so that bonding can be achieved in the steam presses extensively used in the apparel making process. Activation in presence of steam is generally achieved at temperatures below the melt point of the fibers, hence low enough to prevent damage to synthetic fabrics. Also, the steam easily penetrates the fabric, reaching the bond line quickly.

The water absorption of nylons generally decreases as the length of the carbon chain increases. Thus we see from Table 7 that the higher nylons absorb less water than the lower nylons. Also, the even-numbered nylons absorb less water than the odd-numbered nylons. Absorption of moisture results in a slight decrease in tensile strength, a major increase in ultimate elongation, and a corresponding decrease in flexural modulus, as shown in Table 8.

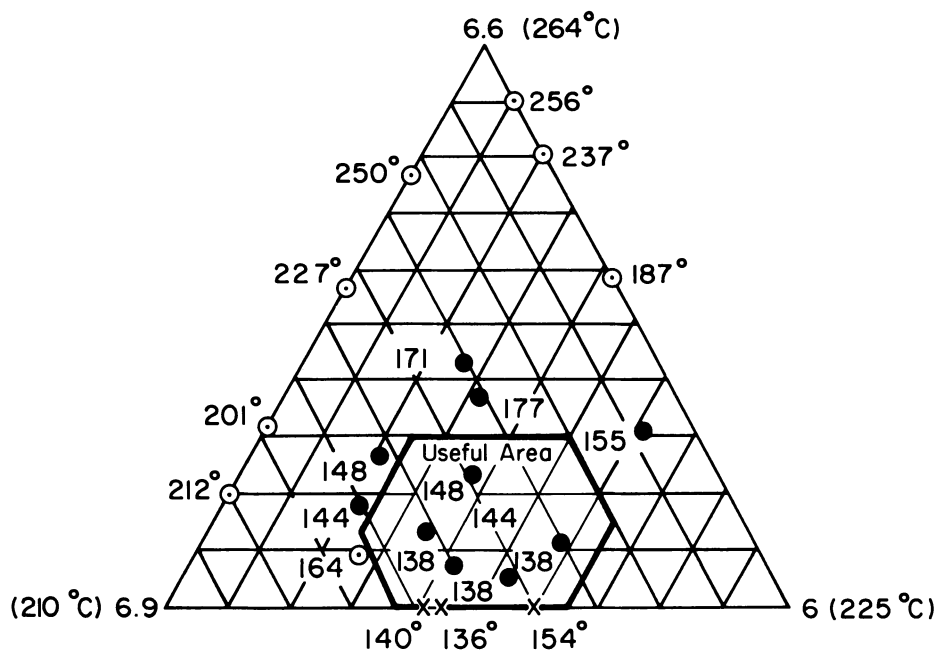


Fig. 3.

**Table 7. Water Absorption Characteristics of Nylons.**

<i>Conditions</i>	<i>6-6</i>	<i>6</i>	<i>6-10</i>	<i>6-12</i>	<i>11</i>	<i>12</i>
24 hrs, 100% RH, 73°F, %	1.5	1.6	0.4	0.4	0.3	0.25
Equilibrium, 50% RH, 73°F, %	2.5	2.7	1.5	1.5	—	—
Saturation, 100% RH, 73°F, %	9.0	9.5	3.5	3.0	1.9	1.4

**Table 8. Effect of Moisture (Equilibrium) on Key Properties of Nylon.**

<i>Type of Nylon</i>	<i>Ult. Tensile Strength, 10<sup>3</sup> psi</i>		<i>Ult. Elongation, %</i>		<i>Flex. Modulus, 10<sup>3</sup> psi</i>	
	<i>Dry</i>	<i>50% RH<sup>a</sup></i>	<i>Dry</i>	<i>50% RH<sup>a</sup></i>	<i>Dry</i>	<i>50% RH<sup>a</sup></i>
6-6	12.0	11.2	60	300	410	175
6	11.8	10.0	200	300	395	140
6-10	8.5	7.1	20	220	285	160
6-12	8.8	7.6	150	340	290	180
11	8.0	7.6	120	330	170	150
12	8.0	7.6	250	270	180	165

<sup>a</sup>Equilibrium.

Since adhesives used in fabric bonding are subjected to washing and dry cleaning, it is evident that a balance of steam activation and wash resistance must be achieved. Resistance to hot water washing varies with the composition of the polyamide. The easier the hot melt activates with steam, the poorer the resistance to wash. Many dry cleanable garments have poor wash resistance, particularly at temperatures above 140°F.

On the other hand, one can synthesize polyamides which have good wash resistance and dry cleaning, but do not activate as easily with steam. Polyamides with the same melt point but with different resistance to wash and steam activation are available commercially. For example, the following two polyamide terpolymers with the same melt point have very different activating temperatures and resistance to hot water wash:

Polyamide	M.P.	Activation Temp. with Steam	Max. Hot Water Water Resistance	Dry Cleaning Resistance
Nylon 6, 6-6, 6-9	150°C	105°C	50°C	excellent
Nylon 6, 6-9, 6-12	150°C	135°C	95°C	excellent

The major suppliers of nylon terpolymers are Bostik Division of Emhart Corp., Emser-Werke, and Rilsan Corp., Div. of Atochem.

The properties of typical polyamides are shown in Tables 9–11.

These fabric adhesives are available in several forms, most commonly as powders, pellets, films, spun-bonded webs and monofilaments.

*Powders* are available in various particle size ranges, e.g., 0–74 microns, 74–210 microns, 210–400 microns. Powders are applied to both nonwoven and woven interface fabrics. They are sold to garment manufacturers for bonding to various parts of garments to improve appearance both before and after dry cleaning and washing. Many sewing operations are thus eliminated. Also, lower weight shell fabrics can be used to produce garments of better quality.

The 0–74 micron powder is dispersed in water, with the addition of dispersing agents and binders, such as acrylic latex or VA-E (vinyl acetate-ethylene) latex. The resultant paste

is applied to the interface fabric through a perforated cylinder, dried and partially fused.

The 74–210 micron powder is applied by the

**Table 9. Bostik Hot Melt Polyamides.**

<i>Property</i>	<i>4214</i>	<i>4222</i>	<i>4232</i>	<i>4930</i>
Specific gravity	1.085	1.08	1.095	1.07
Melt point range:				
Ring and ball, °C	130	130	135	152
DSC <sup>a</sup> melt point, °C	110	102	115	135
Viscosity, cps, 180°C	425,000	190,000	300,000	325,000
Tensile at break, psi	6,000	5,000	7,500	7,500
Elongation at break, %	500	600	450	350

<sup>a</sup>Differential scanning calorimeter.**Table 10. Rilsan Platamid Resins.**

<i>Property</i>	<i>H105P</i>	<i>H165P</i>	<i>H003P</i>	<i>H005P</i>	<i>H006P</i>
Specific gravity	1.08	1.10	1.05	1.08	1.09
Melt point range, °C	115–125	105–115	105–115	115–125	145–150
Start of adhesion, °C	115	90	90	115	140
Moisture absorption, 68°F, 65% RH, %	3.5	2.0	2.0	3.5	2.0
Max. moisture absorption in water, 20°C, %	10.0	6.0	6.0	10.0	6.0
Viscosity, ps, 150°C	21,000	5,600	5,200	8,200	3,200 (160°C)
Characteristics	High Visc.	Low Visc. Plasti- cized High Flexibility	Low Visc.	Medium Visc.	Low Visc.

**Table 11. Emser Werke Giltex Polyamides.**

	<i>1P</i>	<i>2P</i>	<i>4P</i>	<i>5P</i>
Melting temperature range, °C	110–120	120–130	105–115	80–85
Melt viscosity, Poise, 160°C	7,000	5,000	1,000	1,300
Melt index, g/10 min, 160°C	14	20	100	75
Moisture absorption, %	2.5	2.5	2.0	2.5
Glueline temperature, °C	140–160	140–160	120–140	95–120
Pressing time, sec	12–20	12–20	10–15	10–15
	fusible	not	fusible	not
	with	fusible	with	fusible
	steam	with	steam	with
		steam		steam
Reactivated with steam	yes	no	yes	no
Dry cleaning resistance, perchloroethylene	very good	very good	very good	very good
Resistance to laundering, °C	60	95	40	40
Applications	fusing of all front parts	for hot laundrying resistant bonding	for pressure and temp. sensitive lace fab- rics, edge bonding	bonding of leather hides and fur



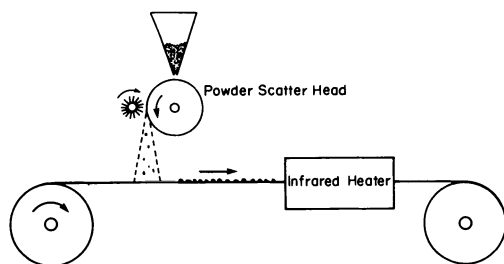


Fig. 4. Powder scatter process.

dry powder dot process (gravure roll) and fused under infrared heaters; then the interface fabric is cooled and rolled for sale to the garment industry. See Fig. 5

The coarse 210–400 micron powder is applied to the interface fabric by scattering uniformly, then fused onto the fabric with infrared heaters; then the fabric is cooled, calendered, and rolled. See Fig. 4.

In all cases, a fabric containing isolated dots of adhesive is the final product. The discontinuous pattern contributes to the soft hand of the fused fabric. The closer the dots, the firmer is the resulting hand.

*Film* is obtained by extruding terpolymers such as nylon 6, 6–6, 12 (Rilsan, Emser-Werke) or nylon 6, 6–9, 6–12 (Bostik) on re-

lease paper. The film is used for bonding labels, decals, etc. onto garments.

*Spun bonded* nylon forms a *nonwoven* web used for fabric bonding in clothing factories and available in notion stores in different widths and weights for home sewing. Webs of this type are available from Bostik and Pellon Corp.

*Pellets*, like powders, are printed in dot patterns on fabrics by the Rototherm hot melt process described below. The adhesive-printed fabrics are used in apparel manufacturing or for continuous lamination of fabrics to other substrates.

The manufacturers of polyamides offer them in various forms. Rilsan Corp. supplies the basic nylon polymers as well as powders and monofilaments. Bostik Fastening Systems Group provides the polymers in pellet form, but also as powder, spun bonded web, and film. Emser-Werke supplies pellets and powders.

## POLYESTERS

Polyesters are the reaction product of dibasic acids with polyfunctional hydroxyl-bearing materials. Both the linear saturated polyesters and the unsaturated polyesters have achieved commercial significance.

The *unsaturated* polyesters are oligomers

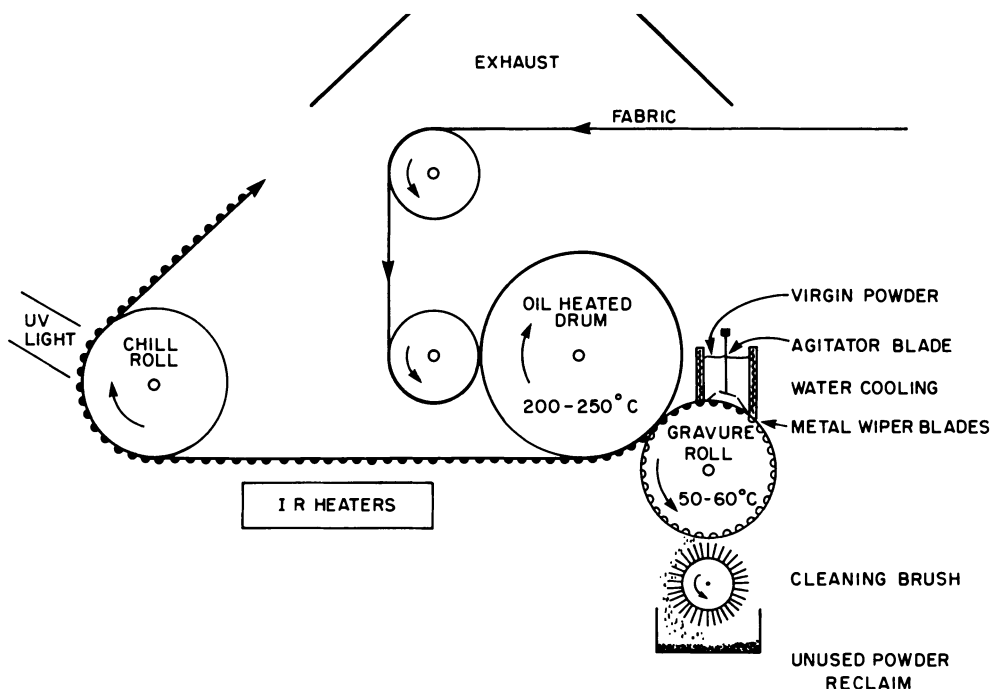


Fig. 5. Powder point printer.

made from diols and unsaturated dibasic acids, generally maleic anhydride. These low molecular weight polymers are cured to highly cross-linked networks by reacting with unsaturated monomers, usually styrene, in the presence of peroxide catalyst. Reinforced with fiberglass, they constitute the fiber-reinforced polyesters (FRP).

The *linear saturated* polyesters comprises a large class of polymers with a variety of properties. The main types are:



**Class A:** Fiber grade or engineering type polyesters with high melt point and molecular weight, derived wholly from aromatic diacids, diols, and hydroxy acids.

**Class B:** Low molecular weight polyesters derived from aliphatic dibasic acid

urated polyesters with melt point between the Class A (fiber grade) and the Class B polyesters.

It is this last class of polyesters that finds use in hot melt adhesives. The compositions and properties of the available polyesters varies widely and fall between Class A and Class B polymers; typically they are derived from aliphatic diols and aromatic diacids, notably terephthalic acid, and are synthesized to fairly high molecular weight, between 10,000 and 30,000.




The high melt points of the terephthalate polyesters are due to the chain stiffening effect of the *p*-phenylene group. This can be demonstrated by comparing terephthalate polyesters with the corresponding adipate polyesters, which contain the same number of carbon atoms:

		$I_m, ^\circ\text{C}$
$\text{—O(CH}_2)_2\text{—OC—}$  $\text{—CO—}$	Poly(ethylene terephthalate)	265
$\text{—O(CH}_2)_2\text{—O—OC(CH}_2)_6\text{CO—}$	Poly(ethylene adipate)	45
$\text{—O(CH}_2)_4\text{—O—OC—}$  $\text{—CO—}$	Poly(butylene terephthalate)	225
$\text{—O(CH}_2)_4\text{—O—CO(CH}_2)_6\text{CO—}$	Poly(butylene adipate)	42

and excess diol. Suitable as intermediates in the synthesis of polyurethanes, they are usually viscous liquids of molecular weight 1,000–3,000.

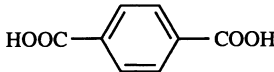
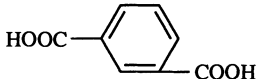
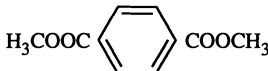
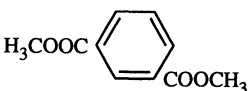
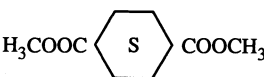
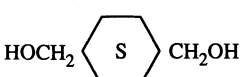
**Class C:** High molecular weight linear sat-

The position of the carboxyl group on the phenylene also has a great influence on the melting point of the polymer. For example, for polyesters derived from ethylene glycol and the three phenylene dicarboxylic acids, the melt point is:

		$T_m, ^\circ\text{C}$
	+ Ethylene glycol → Poly(ethylene terephthalate)	256
	+ Ethylene glycol → Poly(ethylene isophthalate)	103
	+ Ethylene glycol → Poly(ethylene phthalate)	78

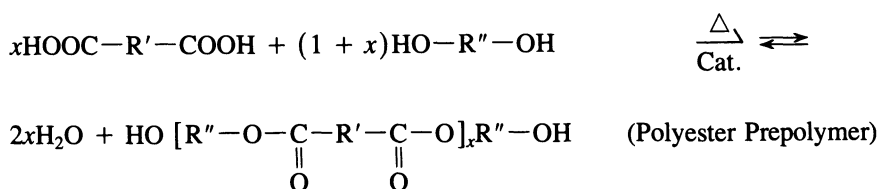
Poly(ethylene terephthalate) (PET) is widely used in fibers and films. Sometimes a small amount of isophthalic acid is included to modify the properties.

The polyesters for hot melts are generally polymers of more than one acid and one or more glycols. The major monomers and their properties are listed below:

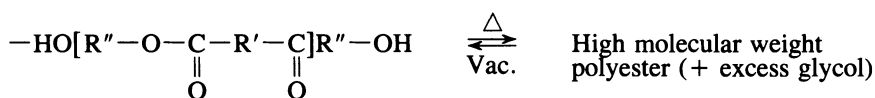
Acids		Melt Point, °C	Molecular Weight
Terephthalic acid		Sublimes @ 300°C	166
Isophthalic acid		348	166
Adipic acid	$\text{HOOC}(\text{CH}_2)_4\text{COOH}$	149	142
Azelaic acid	$\text{HOOC}(\text{CH}_2)_7\text{COOH}$	106	188
Sebacic acid	$\text{HOOC}(\text{CH}_2)_8\text{COOH}$	133	202
Dimer acid	Structures shown earlier in chapter		
<i>Dimethyl Esters</i>			
Dimethyl terephthalate		140.8	194
Dimethyl adipate	$\text{H}_3\text{COOC}(\text{CH}_2)_4\text{COOCH}_3$	8.5	170
Dimethyl azelate	$\text{H}_3\text{COOC}(\text{CH}_2)_7\text{COOCH}_3$	—	216
Dimethyl sebacate	$\text{H}_3\text{COOC}(\text{CH}_2)_8\text{COOCH}_3$	26.4	230
Dimethyl isophthalate		68.0	194
1,4-Cyclohexane dimethanol		50	200
<i>Glycols</i>			
Ethylene glycol	$\text{HOCH}_2\text{CH}_2\text{OH}$	12	62
1,4-Butanediol	$\text{HOCH}_2\text{CH}_2\text{CH}_2\text{OH}$	20	90
1,6-Hexanediol	$\text{HO}(\text{CH}_2)_6\text{OH}$	42	118
1,4-Cyclohexane dimethanol		—	164

In the synthesis of polyesters, either the free acids or their methyl esters are used. The reaction is carried in two stages:

1st Stage:



2nd Stage:



In the first stage the acid or acids are reacted with an excess of glycols at temperatures between 200°C and 240°C, generally in the presence of a catalyst, to produce a low molecular weight prepolymer plus water or methyl alcohol byproduct. This reaction can be carried at atmospheric pressure or under pressure. An esterification catalyst such as zinc acetate is chosen when acids are used to make the prepolymer, and a transesterification catalyst such as tetraisopropyl titanate when dimethyl esters are employed.

In the second stage, the polycondensation reaction proper, the prepolymer is heated to 240–270°C under high vacuum in the presence of a transesterification catalyst.

The reactions are speeded by removing the byproducts, water or methanol in the first stage and excess glycol in the second stage. This is accomplished by purging the reaction with inert gas in the first stage and applying vacuum in the second stage.

Many catalysts are mentioned in the literature for making polyesters. The most commonly used are: lead acetate, sodium acetate, calcium acetate, zinc acetate, organotin compounds, titanium esters, antimony trioxide, and germanium salts.

The choice of catalysts depends on the monomer and also on the application for the adhesive. For example, if the adhesive is to be used in food packaging, the catalyst chosen would be one which meets FDA approval, e.g. the acetate of sodium, calcium or zinc.

Like polyamides, the polyester homopolymers are seldom used in hot melts. In most cases a better balance of properties such as melt point, flexibility, rate of crystallization, etc. is achieved with copolymers. As in polyamides, copolymerization can yield copolymers with a wide range of properties. Some copolymers have melt points below that of the lower melting homopolymer. Examples of copolymers with eutectics are shown in Figs. 6 and 7.<sup>9</sup>

The physical properties of the copolymers vary with melt point. The copolymers are more flexible as the composition approaches the eutectic point. Indeed, copolymers around the 50/50 mole ratio of terephthalic/sebacic acid are elastomeric in nature, and were extensively studied by DuPont as elastic fibers. Eutectics are also observed in ethylene terephthalate/adipate and butylene terephthalate/sebacate copolymers. Introduction of an additional monomer, for example, sebacic acid or azelaic acid in butylene terephthalate/isophthalate polymers, results in further modification of the properties. In general, introduction of the aliphatic chains results in lowering of the melting point, increased flexibility, greater adhesion properties, and in the case of crystalline polyesters, a faster crystallization rate.

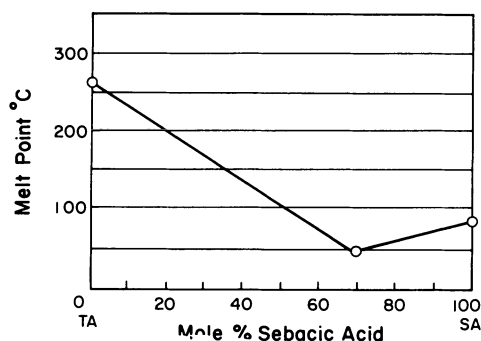


Fig. 6. Ethylene terephthalate/sebacate copolymers.

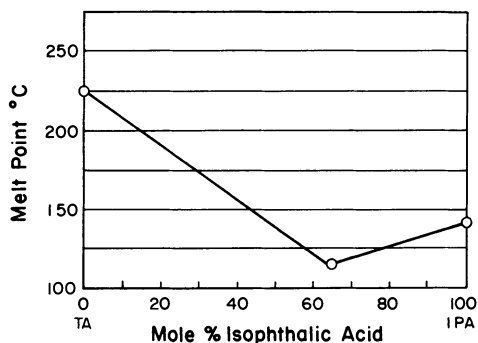


Fig. 7. Butylene terephthalate/isophthalate copolymers.

Plotting of terpolymers in three-component diagrams results in trends similar to those observed in the nylon terpolymers.

Polyesters for hot melts are either crystalline or amorphous. In the crystalline polyesters, the rate and degree of crystallization is greatly affected by the composition; the more regular the chain structure, the faster is the crystallization rate.

The crystalline polymers are derived from the more symmetric acids such as terephthalic acid and straight chain diols. The longer the carbon chain of the diol, the lower the melt point and glass transition temperature and the faster the rate of crystallization.

An even number of carbon atoms in the glycols gives higher melt points as well as more crystalline and faster crystallizing polyesters:

	$T_g$ , °C	$T_m$ , °C
Ethylene terephthalate (PET)	80	256
1,3-Propanediol terephthalate	—	217
1,4-Butanediol terephthalate	—	222
1,6-Hexanediol terephthalate	—	148

The lower melt point and glass transition result from the reduction in chain stiffness provided by the longer chains in the higher molecular weight diol.

The same effect is obtained when one copolymerizes long chain dibasic acids with terephthalic acid. For example, the ethylene glycol copolyesters of terephthalic acid and sebacic acid, in addition to having lower melt points, crystallize much faster at room temperature because of the increased mobility provided by the flexible molecules.

The crystallization of the polymers can be detected by several changes in properties: development of opacity, increase in modulus, reduction in elongation, shrinkage, increase in specific gravity.

The temperature at which the change to the crystalline form takes place is dependent on the composition of the copolymers, but is always higher than the glass transition temperature. Some of the copolymers can crystallize at room temperature while others must be heated or cooled to accelerate the rate of crystallization.

For the faster crystallizing polymers, the op-

timum crystallization temperature can be obtained by running differential thermal analysis on samples which have been quenched in the amorphous state. With this technique, one can measure the glass transition, the crystallization temperature and the crystalline melt point. For example, a sample of amorphous PET would show first the glass transition at 81.8°C followed by a crystallization exotherm at 164.3°C and a crystalline melt point ( $T_m$ ) at 251.5°C. See Fig. 8.

Generally, higher crystallinity results in sharper melt points. This is important in an adhesive, as the crystalline polymers retain their properties until the melt point is reached.

Crystalline polymers generally are not as soluble as amorphous polymers and thus have better solvent resistance. The appearance of these polymers in the crystalline state is opaque.

The amorphous polymers are derived from monomers which have side groups, such as neopentyl glycol, or multipolymers which have very little chain regularity and thus are unable to crystallize.

These polymers, which are in most cases clear, have a broader melt point range, are more soluble, and hence are less resistant to solvent attack.

The shrinkage which results during crystallization sometimes has a deleterious effect on the bonds. It is important, therefore, that the bonds made be evaluated after the crystallization has taken place. Amorphous polymers also shrink on cooling, but far less.

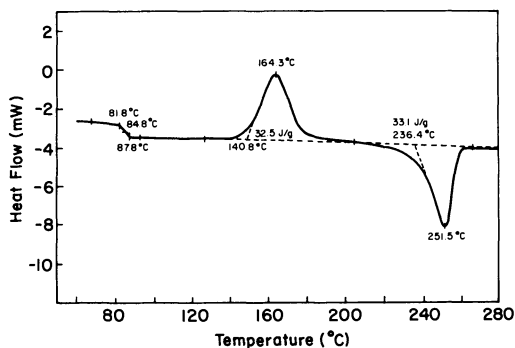


Fig. 8. DSC thermogram of polyethylene terephthalate showing the three major phase transitions; glass transition ( $T_g$ ) at 81.8°C, crystallization starting at 140.8°C, and crystalline melt point ( $T_m$ ) 251.5°C. (Courtesy the E. L. DuPont de Nemours and Company).

There are several manufacturers of polyesters for hot melts. The major suppliers in the United States are Bostik Fastening Systems Group, Goodyear Chemicals, Eastman Chemical, and Whittaker Corp. (successor to DuPont). The main products of these suppliers are shown in Tables 12–15.

European suppliers include: Emser-Werke (see Table 16), Dynamit Nobel, and Huels.

Polyester hot melts are in most cases high molecular weight products with high melt viscosity. Because of this, they are applied at higher temperatures than the olefin polymer hot melts, and with equipment able to handle high viscosity.

Because polyesters tend to be hydrolyzed by the presence of water at the application temperature, it is usually recommended that the products be dried prior to melting. To minimize hydrolysis, application equipment which reduces the residence time in the molten state

is recommended. Preferred equipment are screw extenders and hot grid bulk melters which melt only the product in contact with the grid.

Polyesters, unlike polyamides, have little tendency to char when held in the molten state for a long time. Instead, they decline in viscosity and molecular weight. To avoid reduction in properties, polyesters should be exposed to the lowest possible application temperatures and the shortest dwell time in the melt equipment. Failure to prevent hydrolysis of the hot melt can result in very dramatic deterioration in the properties of the ultimate bonds.

### Uses

Polyesters are used as adhesives in two ways:

1. The polyester hot melt is applied and the two substrates are immediately put together to form a bond.

**Table 12. Bostik Hot Melt Polyesters.**

<i>Property</i>	<i>7102</i>	<i>4101</i>	<i>7106</i>	<i>4117</i>	<i>7199</i>	<i>4177</i>	<i>4156</i>	<i>7116</i>
Color	lt. tan	lt. tan	straw	off-white	off-white	off-white	off-white	lt. tan
Form	granules	pellets	granules	pellets	granules	pellets	pellets	granules
Melt Range								
°F	200–248	248–271	245–260	282–288	344–350	356–360	309–314	
°C	94–120	120–133	118–127	136–142	173–176	180–182	154–156	
Morphology	cryst.	cryst.	amorph.	cryst.	cryst.	cryst.	cryst.	cryst.
Setting speed	slow	moderate	moderate	moderate	v. fast	v. fast	fast	moderate
Specific gravity	1.25	1.27	1.25	1.28	1.28	1.25	1.28	1.25
Acid No., mg KOH/g	1–2	2–4	—	1–2	—	—	—	—
Hydroxyl no., mg KOH/g	1–4	2–4	—	2–3	—	—	—	—
Glass transition, °C	–5	–5	5	–6	–2	–3	–9	–6
Melt Visc., 215°C	70,000	40,000	50,000	220,000	20,000	24,000	27,000	20,000
Tensile, psi	2,500	3,400	1,500	4,700	2,000	2,500	3,500	3,500
Elongation, %	700	570	250	400	200	300	400	400

**Table 13. Eastman Hot Melt Polyesters.**

<i>Property</i>	<i>FA-250</i>	<i>FA-252</i>	<i>FA-300</i>
Physical form	pellets	pellets	pellets
Color	white	white	white
Density	1.25	1.28	1.24
Melt point	212°F	230°F	266°F
Melt visc., 210°C	100,000	140,000	96,000
Inherent visc.	0.72	0.85	0.72

**Table 14. Whittaker (Formerly DuPont) Solid Polyester Adhesives.**

<i>Code</i>	<i>49000</i>	<i>49001</i>	<i>49002</i>	<i>49003</i>
Appearance	tough, hard, amber colored, nontacky at 77°F	soft, plastic light gray color, slightly tacky at 77°C	very tough, flexible, light gray color, nontacky at 77°F	tough, flexible, light gray color, nontacky at 77°F
Odor	none	none	none	none
Specific gravity	1.33	1.28	1.23	1.17
Flow melt point range, °F(°C)	245–275 (118–135)	110–170	260–300	190–230
Tensile strength, 77°F, psi	1500–2500	—	1000–1500	—
Elongation, 77°F, %	600–1000	>2000	500–1500	>2000
Color stability	excellent	excellent	excellent	excellent
Acid number	0.5–2.5	0.5–2.5	0.5–2.5	0.5–2.5
Hydroxyl number	5.0–15.0	5.0–15.0	5.0–15.0	5.0–15.0
Dielectric strength, Volts/mil	2700	—	3200	—
Bond strengths, 180° Peel, 77°F, lb/in.				
3 mil Mylar/Mylar at 0.2–0.3 dry mil adhesive	4–6	4–6	4–6	4–6
3 mil Mylar/copper foil at 0.4–0.5 dry mil adhesives	6–8	4–6	6–8	4–6

**Table 15. Goodyear "Vituff" Hot Melt Polyesters.**

<i>Product</i>	<i>Typical Characteristics</i>	<i>Melt Point</i>	<i>Appl. Temp.</i>	<i>Appl. Viscosity, Poise</i>	<i>Setting Speed</i>	<i>Glass Transition Temp. (t<sub>g</sub>), °C</i>	<i>Dead Load Strength Al/Al kg.</i>
VFR 4302	Strong bonds to leather, vinyl, urethane, and other porous substrates. High temperature resistance and very sharp melt point.	207	240	94	Very fast	–10°C	250°F
VFR 4444	Less rigid than 4302. Combines fast set time with excellent bonds to porous substrates.	190	220	770	Fast	30°C	250°F
VFR 4751	Lower viscosity version of 4444. Fast setting adhesive with high temperature service level.	185	220	240	Fast	30°C	250°F
VFR 5126	Strong, flexible adhesive with outstanding solvent and water resistance. Recommended for textile applications.	174	220	670	Moderate	–2°C	200°F
VFR 4980	Tough, flexible adhesive that provides strong bonds to a wide variety of substrates. Adhesive can be heat reactivated at moderate temperature.	124	220	770	Slow	22°C	170°F
VFR 5125	Very flexible, tough material. Bonds well to metal (preheated) and most thermoplastics, such as vinyl, polycarbonate (Lexan) Phenylene oxide (Noryl), ABS, Nylon, and polyester.	115	210	130	Slow	–9°C	155°F

Table 15. (Continued)

Product	Typical Characteristics	Melt Point	Appl. Temp.	Appl. Viscosity, Poise	Setting Speed	Glass Transition Temp. ( $t_g$ ), °C	Dead Load Strength Al/Al kg.
VAR 5898	Higher melting version of 5125. Outstanding bonds to wood, metal (preheated) and most thermoplastics. Excellent general purpose high performance adhesive.	123	218	185	Mod- erate	-20°C	225°F
VAR 5899	Lower melt viscosity version of 5898. Longer open time for difficult product assembly applications. General purpose high performance hot melt.	130	204	90	Mod- erate	-8°C	225°F
VAR 5893	Combines flexibility with sharp melting point. Excellent bonds to most porous substrates with a high temperature service level.	200	240	100	Very fast	-10°C	250°F
VAR 5831	Extremely flexible adhesive with outstanding bonds to metal (preheated) and thermoplastics. Recommended for bonding thermoplastic films. PET (Mylar), (Tedlar), polyurethane, vinyl, moderate temperature service level.	149	218	250	Slow	-10°C	150°F
VMF 400	Rigid noncrystalline adhesive with outstanding bonds to metal (preheated) and plastics. Meets most FDA requirements for packaging adhesives.	185	240	5,000	Slow	66°C	160°F
VMF 415	Flexible, tough, noncrystalline adhesive. Excellent bonds to plastic films, PET (Mylar), vinyl.	180	220	2,360	Slow	5°C	160°F
VAR 5825 <sup>a</sup>	Extremely tough, flexible adhesive. Recommended for electrical and textile product assembly applications.	160	220	400	Fast	0°C	220°F
VAR 5821 <sup>a</sup>	High temperature service level. Extrusion-grade recommended for wire coating. More flexible than PET.	220	275	250	Fast	75°C	300°F plus

<sup>a</sup>VAR 5825 and VAR 5821 are polyester blends. The other products are polyesters.

Table 16. Emser Griltex Hot Melt Polyesters.

Property	6G	8G
Physical form	granules	granules
Color	off-white	off-white
Density	—	—
Melt Viscosity, M.P. at 200°C	200,000	150,000
Melt point	130-140°C	105-115°C

- The preformed adhesive in the form of an extruded film, web, powder, etc., is applied to substrate, then later is heat reactivated and pressed to achieve a bond.

In the first category, polyesters serve in the shoe industry to last different parts of the shoe. The adhesives are supplied either in monofilament form or in pellets, melted and applied to



the substrate, then immediately bonded. The adhesives for this application have high melt point, 170–190°C, and are very fast-setting crystalline polyesters. Toe lasting of shoes with polyesters of this type can be accomplished with dwell time of less than two seconds.

High melting, fast crystallizing polyesters, are also being used in continuous laminations of fabric and plastic substrates. The adhesive is melted via an extruder or grid-type bulk melter, then is supplied in molten form to a gravure coating roll. The amount of adhesive applied is determined by the characteristics of the gravure cell, the rheology of the adhesive, and the affinity of the adhesive to the substrate. Controlled deposition of the adhesive is achieved by the design of the pattern and volume of adhesive.

A machine for gravure printing of hot melts has been developed by Rototherm, Anaheim, California. See Figs. 9 and 10. With this process, adhesive is applied to one of the substrates, which is laminated to the second substrate while the adhesive is still hot. Alternatively, in fabric bonding in the apparel industry, the adhesive is applied to one of the substrates and later reactivated by heat to permit lamination to the second substrate.

The other category, preformed adhesives

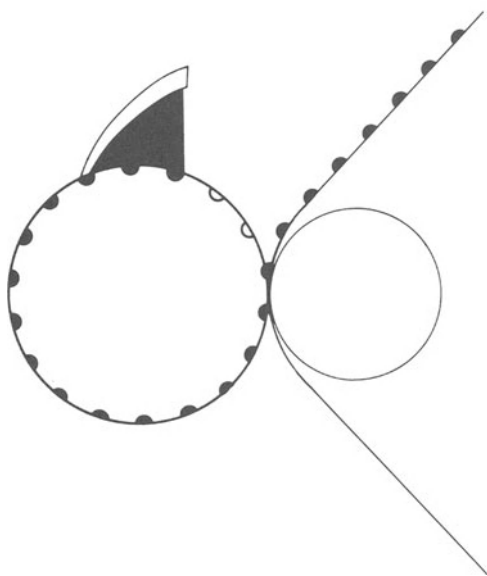


Fig. 9. Rotogravure printing. (Courtesy Rototherm Company, California).

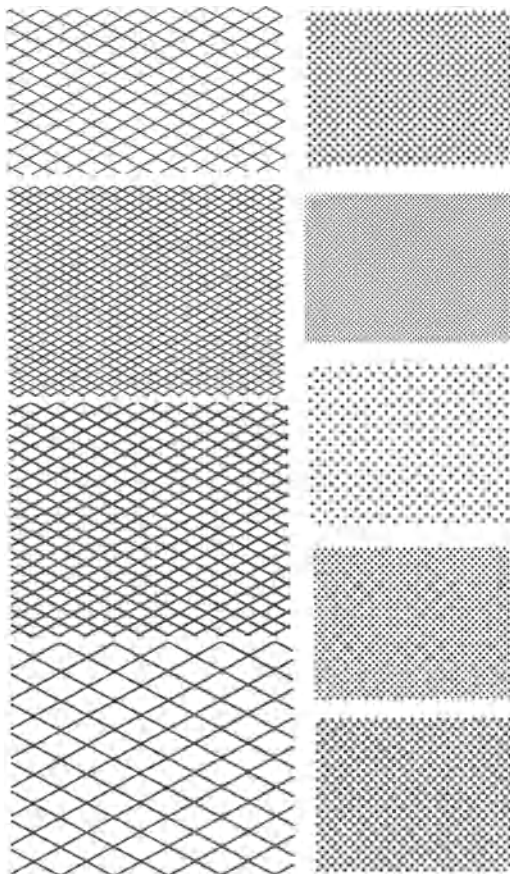


Fig. 10. Typical printing patterns with hot melts (Courtesy of Rototherm Company, California).

such as film, powders, webs, monofilaments, comprises the major part of the polyester hot melts. In this application the adhesive is positioned on the substrate, then a bond is formed with heat and pressure. Extruded film adhesives are used to bond labels, decals, embroideries, etc. to garments with specially designed heated presses.

Adhesives in powder form are applied to woven or nonwoven fabric for the manufacture of women's and men's garments. Powders are also being used for in-line lamination of urethane foam to upholstery fabric by heat activating the applied powder to the foam and laminating to the fabric.

Open mesh polyester adhesive webs are advantageous in the garment industry for reinforcing different parts of the garments.

Hot-melt-type polyesters are being spun into fibers which are mixed with higher melting fi-

bers, acting as the bonding agents in nonwoven fabrics with special properties.

Powdered polyester hot melts also serve as binders for nonwoven fabrics.

Selection of the method of application and the correct adhesive depends on many considerations:

1. Heat stability and properties of the hot melt.
2. Adaptability to production systems.
3. Application temperature and method.
4. Properties of the substrates, heat sensitivity, porosity, etc.
5. Hand desired in the finished laminate.
6. Performance desired of the finished bonds.

Polyesters have some outstanding properties:

1. Adhesion to a variety of substrates.
2. Outstanding adhesion to plasticized vinyl.
3. Excellent water resistance.
4. Excellent heat resistance.
5. Low temperature flexibility.
6. Very good UV resistance.
7. Excellent electrical properties.
8. Good resistance to oil and grease.

Some limitations are:

1. Specialized equipment needed for application.
2. Limited resistance to hydrolysis at high temperatures.

## Compatibility

Polyester hot melts are generally used uncompounded. However, compounds containing polyurethanes, polyethylene, hydrocarbon resins, etc. for specific objectives, have been reported in the patent literature.

## POLYESTER AMIDES

Many polyester amides have been reported in the literature, and several patents have been issued.

One of the developments that has been widely publicized is the development of polyester amides by Monsanto. According to U.S. Patent 3,650,999, these copolymers, trade named Montac, are made by reacting an aromatic polyester, such as PET or PBT, with dimer acid to form an acid-terminated prepolymer which is then reacted with a diamine to produce blocked polyester-amides with melt points, flexibility, and unique adhesive characteristics suitable for structural adhesives.<sup>10</sup> These block copolymers have a crystalline block derived from the polyester and an amorphous block derived from the polyamide. Typical properties of copolymers mentioned in the patents are shown in Table 17.

These adhesives have been promoted for bonding SMC automotive parts. Bonds equivalent to two-part adhesive systems such as two-part polyurethanes and epoxies are being claimed. Using Montac 5500 with a crystalline

**Table 17. Poly(Ester-Amide) Block Copolymers, Examples 1–7, U.S. Patent 3,650,999**

Property	1	2	3	4	5	6	7
% Crystalline polyester (PET)	30	60	60	60	30	60	60
% Polyamide	70	40	40	40	70	40	40
Tensile strength, psi	750	3,300	3,000	3,100	1,600	2,800	3,900
Elongation, %	490	370	300	500	450	310	290
Inherent viscosity	0.75	0.68	0.61	0.59	0.89	0.67	0.79
Crystalline M.P., °C	174	185	205	155	168	196	185
Bond Strength, psi,							
Steel/Steel	985	1,620	2,300	1,700	1,410	2,340	1,590
Aluminum/Aluminum	1,140	1,620	1,800	1,760	1,500	2,040	1,000
Creep resistance, hr	> 192	> 192	> 174	> 174	> 186	168	< 100
Extractables (toluene/iso-propanol), %	< 1	< 1	< 1	< 1	< 1	< 1	
Ratio, aromatic polyester to aliphatic polyamide	30/70	60/40	60/40	60/40	30/70	60/40	60/40

**Table 18. Characteristics of Monsanto's "Montac" Resin.**

Typical Montac Resin Properties						
Resin Type	Specific Gravity	Glass Transition Temperature <sup>a</sup>	Crystalline Melting Point <sup>a</sup>	Polymer Tensile Strength <sup>b</sup>	Polymer Elongation <sup>b</sup>	Melt Viscosity @ 249°C (480°F)
Montac 5500	1.20 g/cc	35°C	207°C	4,000 PSI	420%	70,000 cps
Montac 5550	1.13 g/cc	-15°C	168°C	2,000 PSI	600%	55,000 cps
Typical Bond Performance 25°C/77°F: Steel/Steel						
Resin Type	Lap Shear Tensile Strength <sup>c</sup>	T-Peel <sup>d</sup>	Creep Resistance <sup>e</sup> 5-lb. Load (1" × 1" Overlap)			
Montac 5500	2,800 psi	1 ppiw	168 hrs. @ 150°C			
Montac 5550	1,600 psi	35 ppiw	168 hrs. @ 150°C			
Adhesion to Various Substrates						
Excellent	Good to Excellent			Fair		
steel, aluminum	glass reinforced polyesters			some rubber		
glass	(e.g., SMC's, HMC's)			chrome plated		
ceramic	systems using "Nyrim"			high pressure melamine laminates		
leather	urethane RIM					
wood	polycarbonate/PBT blends,					
particle board	ABS					
	nylon polyester					
	PVC					
Excellent environmental resistance to: moisture, humidity, most solvents, ultraviolet light, thermal shock, salt corrosion.						

<sup>a</sup>Perkin-Elmer DSC-2<sup>b</sup>ASTM D-63-80 Modified<sup>c</sup>ASTM D-1002-72<sup>d</sup>ASTM D-1876-72<sup>e</sup>Without bond failure

melt point of 207°C, structural bonds which can be handled in 30 seconds are claimed. This fast bond development reduces the need for fixturing and reduces cycle time. It is claimed, also, that the improved productivity makes these high-priced adhesives cost competitive with two-part adhesives.

Monsanto supplies two main polymers, whose properties are listed in Table 18.

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# High Temperature Organic Adhesives

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## INTRODUCTION

High temperature organic adhesives are required for joining metals, ceramics, plastics, and composites to themselves and to each other. These adhesives, and other materials that are required to exhibit good adhesion, are needed for use in a variety of applications in the aerospace, automotive, computer, electrical, household, and oil industries. The common requirement is thermal stability; but stability under other environmental conditions is also needed. In some applications, the use temperature is not the determining factor. Stability at high temperatures encountered during various processing steps (e.g., soldering) to fabricate a component is the important requirement. These processing temperatures can be significantly higher than the actual use temperature. In this article, high temperature organic adhesives are defined as materials that exhibit usable strength after long term aging (i.e., thousands of hours) at 232°C or short term exposure (i.e., minutes) at 538°C and higher.

High temperature adhesives are required to exhibit a unique combination of properties. This combination will vary from one applica-

tion to another. It is virtually impossible to have all of the desirable characteristics in one system because of the chemistry involved. For example, with the present state of development of high temperature polymers, a high temperature structural adhesive system cannot offer the combination of tack and drape in the tape as well as no volatiles. Some of the major items desired in a high temperature structural adhesive are listed below:

- Adhesive tape with tack and drape
- Processability under moderate conditions with no or little volatile evolution
- Compatibility with various adherends and surface treatments
- Mechanical performance under intended use conditions (temperature, stress, environment)
- Reproducibility and reliability
- Repairability
- Low cost

Other important parameters that demand attention for the successful development of a high temperature adhesive include the following:

- Polymer—purity, molecular weight and molecular weight distribution, glass transition temperature ( $T_g$ ) or heat deflection temperature (HDT), and flow characteristics

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The use of trade names or manufacturers does not constitute an official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration.

- Adhesive tape—carrier, finish, filler, drying cycle, thickness, flow, volatile content, and ambient temperature stability
- Adherend—type, surface treatment, and primer
- Bonding conditions—time, temperature, and pressure

Specific examples are presented to familiarize the reader with some of the stringent requirements for various applications. A favorable combination of processability, performance and price is obviously of utmost importance. Structure adhesives for use in sandwich structures in high speed aircraft should provide good filletting around the cells and high mechanical properties for the long term after thermal cycling under stress over a temperature range of  $-54$  to  $232^{\circ}\text{C}$ , and should be resistant to airplane fluids and solvents. A thin insulating film adhering to a ceramic substrate as used in microelectronics/computers should have a low dielectric constant, low coefficient of thermal expansion, and stability for several hours in an inert atmosphere at processing temperature as high as  $400^{\circ}\text{C}$ . Nonstick interior coating and decorative exterior coating on cookware should adhere to the aluminum substrate, exhibit abrasive and scratch resistance, be stable to cooking temperatures and the effects of hot oils and soaps. Composite matrices which can be construed as adhesives for use in the internal hot working parts of automobile engines (e.g., connecting rods, wrist pins, etc.) should exhibit excellent fatigue and creep resistance, and be amenable to low cost manufacturing. These are a few of the many potential applications for high temperature organic adhesives.

The primary intent of this article is to review the status of experimental and newly developed high temperature organic adhesives with particular attention to aerospace materials. Detailed information on the synthesis of various polymers or bonding conditions can be obtained in the references cited. Several high temperature adhesives are commercially available, and information on these systems can be obtained from the major adhesive suppliers. For aerospace use, these consist primarily of modified epoxy phenolics, toughened bismaleimides, addition and condensation polyimides.

In comparing the performance of the adhe-

sives discussed herein, discretion is advised. Important parameters which influence the performance of an adhesive vary from one evaluation to another. These include polymer properties, carrier, adherend, surface treatment, primer, bonding conditions, aging, and test conditions. Thus, it is difficult to obtain a valid comparison on the performance of polymers as adhesives when the work was done in different laboratories.

## HISTORY

The search for adhesives with mechanical properties and temperature resistance superior to the modified epoxy phenolics developed in the 1950s actually began in earnest in the early 1960s. Many new polymer systems were discovered and evaluated as high temperature adhesives. Condensation polyimides (PIs) evolved as the polymer family which offered the most favorable combination of properties. A few commercially available condensation polyimide adhesive systems were developed, some of which are still currently available. Table I summarizes the historical development of high temperature organic adhesives. The approximate year of introduction refers to the initial report on adhesive performance. The maximum use temperatures for 10 minutes and 100 hours at temperature are reported. In several instances, the maximum 10 minute use temperature was controlled by the  $T_g$ . Some of the polymers could undoubtedly exhibit a higher 10 minute use temperature if they have been exposed to higher temperatures during the fabrication process or a subsequent postcure, hence induced crosslinking. In addition, the adhesive strength of several of these polymers has not been reported at temperatures higher than those listed. Although some of these adhesives have exhibited respectable strength at  $232^{\circ}\text{C}$  in standard ASTM tensile shear specimens (TSS), they may not display comparable performance in other specimen forms (e.g., sandwich specimens) because of factors such as low flow or volatiles evolution.

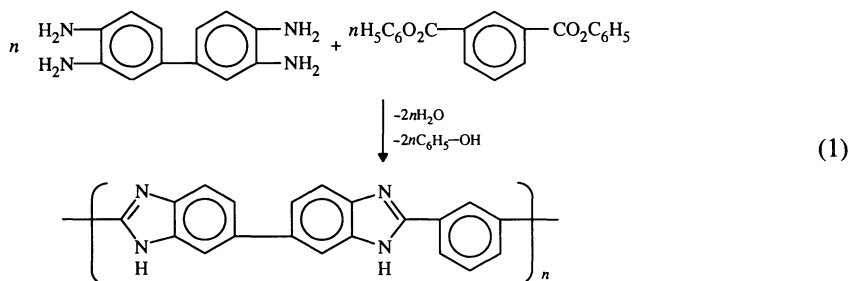
### Benzimidazole Polymers

The first aromatic heterocyclic polymer to undergo extensive evaluation as a high temper-

**Table 1. Development of High Temperature Structural Adhesives.**

Approximate Year of Introduction	Adhesive	Maximum Use Temperature, °C	
		10 min	100 hr
1956	Modified epoxy phenolic	316	232
1964	Polybenzimidazole	538	316
1965	Polyimide	371	316
1970	Polyquinoxaline	538	316
1971	Polyphenylquinoxaline	316	316
1974	Polyarylsulfone	260	260
1975	Acetylene-terminated imide	316	316
1975	LARC-TPI	232	232
1978	Norbornene-terminated imide	316	260
1978	NR-150B type polyimide	316	316
1981	Acetylene-terminated phenylquinoxaline	288	260
1983	Polyphenylquinoxalines with pendent phenylethynyl groups	232	232
1985	Semi-interpenetrating polyimide net- works	232	232
1986	Polyarylene ether	232	232

ature adhesive was a polybenzimidazole (PBI). The chemistry was initially reported in 1961 and involved the reaction of aromatic *bis(o*-diamines) and diphenyl esters of aromatic dicarboxylic acids.<sup>1</sup> The synthesis of a PBI from the polycondensation of 3,3',4,4'-tetraaminobiphenyl and diphenyl isophthalate is shown below:



Most of the high temperature adhesive work on PBIs centered on this particular polymer. In high molecular weight form, this polymer has a  $T_g$  of  $\sim 435^\circ\text{C}$ .<sup>2</sup> It can be compression molded at  $470^\circ\text{C}$  under 2000 psi to provide neat resin specimens<sup>2</sup> or adhesive specimens<sup>3</sup> with high mechanical properties. Obviously these processing conditions are unacceptable for almost all adhesive applications. Because of this, essentially all of the early work on PBI as a high temperature adhesive used a low molecular weight prepolymer.<sup>4</sup> The prepolymer, depending upon the degree of advancement,

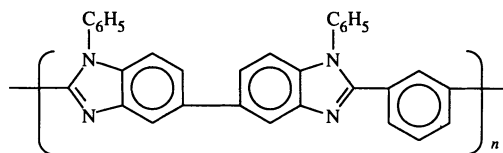
exhibited good flow and accordingly good wetting but required high temperatures to drive the polymerization to completion. A large amount of volatiles (phenol and water) was evolved, which caused processing problems and resulted in porosity in the bondline, especially in large area bonds. In spite of the processing difficulties, good adhesive strengths were obtained

with PBI.<sup>5,6</sup> PH 15-7 molybdenum stainless steel TSS provided strengths of 4000 psi at  $25^\circ\text{C}$ , 2500 and 1100 psi at  $300^\circ\text{C}$  after 100 and 200 hours at  $300^\circ\text{C}$  in air, respectively, and 1100 psi at  $538^\circ\text{C}$  after 10 minutes at  $538^\circ\text{C}$  in air. Many of the aromatic heterocyclic polymers including PBI exhibit good adhesive properties at cryogenic temperature. PBI TSS provided strength of 4600 psi at  $-196^\circ\text{C}$ . In addition, the fatigue resistance ( $10^6$  cycles) of PBI TSS was better at  $-196^\circ\text{C}$  than at  $25^\circ\text{C}$  (2200 vs. 1500 psi).<sup>5</sup>

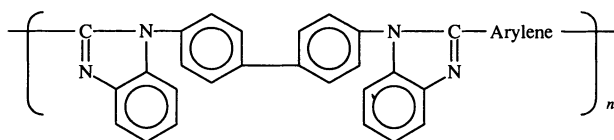
PBI is currently commercially available in the

form of a low molecular weight prepolymer (inherent viscosity of  $\sim 0.05\text{--}0.10\text{ dL/g}$ )<sup>7</sup> and a higher molecular weight polymer (inherent viscosity of  $>0.6\text{ dL/g}$ )<sup>8</sup>

Other types of benzimidazole polymers where the imidazole hydrogen was substituted with a phenyl group<sup>9</sup> or an arylene group<sup>10</sup> such as in structures 1 and 2 respectively have, also been evaluated as adhesives.



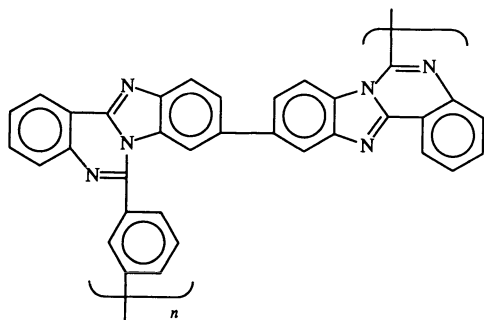
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These polymers are more thermooxidatively stable than the PBI in Eq. (1) but the elimination of the imidazole hydrogen resulted in less intramolecular association and accordingly more thermoplasticity and lower  $T_g$ . The adhesive properties of the polymers in structures 1 and 2 were excellent at  $25^\circ\text{C}$  ( $>4000\text{ psi}$ ) but low at temperatures  $>200^\circ\text{C}$  because of thermoplastic failure.

A variation of a benzimidazole polymer is the polybenzimidazoquinazoline<sup>11</sup> of representative structure 3. In small composites, this ma-



3

terial has shown excellent retention of properties at  $371^\circ\text{C}$  after 200 hours at  $371^\circ\text{C}$

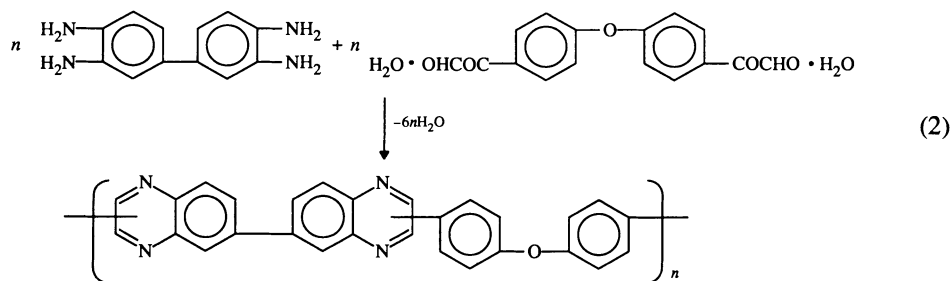
in air.<sup>12</sup> However, cursory evaluation as an adhesive on titanium (Ti, 6A1-4V) adherends gave TSS of  $\sim 3000\text{ psi}$  at  $25^\circ\text{C}$  and poor retention of strength at  $316^\circ\text{C}$ . The low strength of  $316^\circ\text{C}$  was due primarily to improper process conditions and not the thermal properties of the polymer.

Essentially no new adhesive work has been reported on benzimidazole polymers over the

last ten years. These materials, like some other high temperature adhesives to be discussed, are plagued by processing problems due primarily to volatile evolution and the high temperatures required to obtain adequate flow and/or advance the prepolymer. As a class of adhesives, benzimidazole polymers currently available do not exhibit promise for extensive use as high temperature adhesives.

### Quinoxaline Polymers

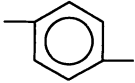
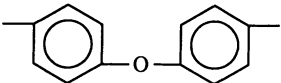
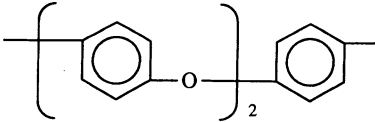
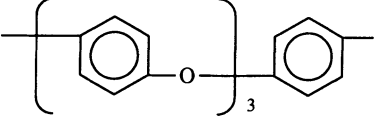
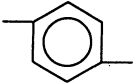

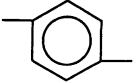
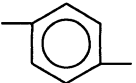
There are two types of quinoxaline polymers: the unsubstituted with no pendent groups on the quinoxaline ring, and the substituted, in which phenyl groups are attached to the quinoxaline ring. The synthesis of the unsubstituted polyquinoxalines (PQ) from the reaction of aromatic *bis(o-diamines)* and aromatic *bis(glyoxals)* was initially reported in 1964.<sup>13-15</sup> The synthesis of a representative PQ from the step-growth polymerization of 3,3',4,4'-tetraaminobiphenyl and 4,4'-oxybis(phenylglyoxal hydrate) is shown in Eq. (2): The  $T_g$ s for a series of PQs are presented in Table 2. The synthesis provides a configurationally unordered polymer with three isomers



distributed randomly within the polymer chain. Because of the isomers, PQs are amorphous and soluble in the ring-closed high molecular

weight form in solvents such as *m*-cresol. The solubility at solids content of 20% (weight/volume) or higher permits the solvent impregna-

**Table 2. Glass Transition Temperatures of Polyquinoxalines.<sup>16</sup>**

$\left( \text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4 \right)_n$		
<i>X</i>	<i>Ar</i>	<i>T<sub>g</sub></i> , °C
—		376
—		305
—		235
—		216
—SO <sub>2</sub> —		342
		318
—O—		206

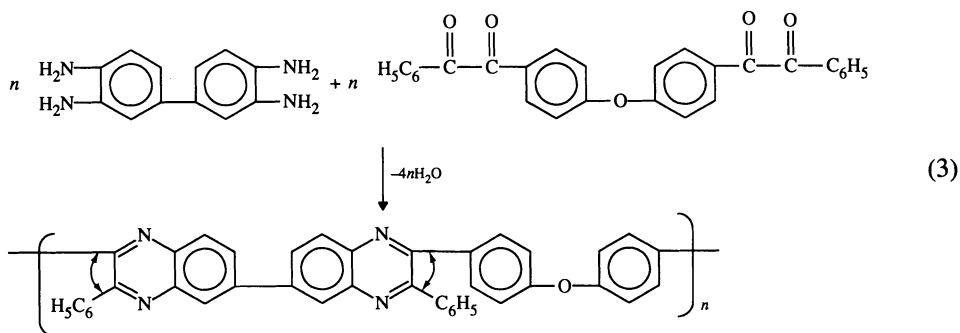


tion of a carrier (e.g., 112 E-glass) and subsequent drying to low volatile content levels. The PQ in Eq. (2) filled with amorphous boron provided the highest 371°C strength reported after aging at 371°C of any organic adhesive. Stainless steel TSS were fabricated from boron filled PQ adhesive tape (112 E-glass) for 1 hour each at 344, 426, and 455°C 200 psi. Strengths of 3350 psi at 25°C, 2280 psi at 316°C after 200 hours at 316°C, 2540 psi at 371°C after 50 hours at 371°C, and 1325 psi at 538°C after 10 minutes at 538°C were obtained.<sup>17</sup> Obviously the process conditions are too stringent for serious consideration of this PQ for extensive use as a high temperature adhesive. When employing processing tempera-

the limited development of these promising polymers as high temperature adhesives.

### Phenylquinoxaline Polymers

The polyphenylquinoxalines (PPQs) are similar to the PQs but offer better solubility, processability, and thermooxidative stability. These polymers are prepared from the reaction of aromatic *bis(o-diamines)* and *bis(phenyl- $\alpha$ -diketones)* as first reported in 1967.<sup>18</sup> Since their initial disclosure, extensive work has been reported on the chemistry, mechanical, and physical properties of PPQs.<sup>19</sup> A representative synthesis shown in Eq. (3) involves the reaction of 3,3',4,4'-tetraaminobiphenyl and 4,4'-oxybis(benzil):



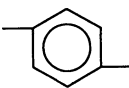
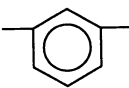
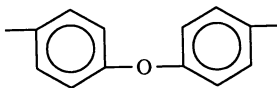
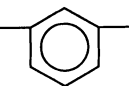

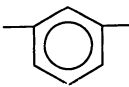
tures of ~400°C, problems are encountered with bagging materials, sealants, malfunctioning of autoclaves and tooling, surfaces degradation of the adherend, residual stresses in the bondline, and thermal degradation of the adhesive.

In spite of the high adhesive strengths at 371 and 538°C obtained for a boron filled PQ, no further work has been reported. This appears to be an area where additional work is worthwhile. The PQ in Eq. (2) had a  $T_g$  of ~300°C but yet in adhesive form, provided high strength at temperatures significantly higher than 300°C. Apparently, crosslinking or interaction with the boron filler occurred at the high processing temperatures to provide a material with temperature performance beyond that of the starting material. PQs are not commercially available; this undoubtedly has contributed to

Table 3 presents  $T_g$ s for several representative PPQs.

Several PPQs have been evaluated as high temperature adhesives<sup>21,22</sup> with the PPQ in Eq. (3) receiving the most attention. As part of the United States Supersonic Transport (SST) program, the PPQ in Eq. (3) was evaluated as a high temperature adhesive for joining Ti to Ti, and Ti to PI and Ti core (sandwich structure), for long term use at 232°C. Ti TSS having a phosphate fluoride surface treatment provided strengths of 4740 psi at 25°C, 3500 psi at 232°C after 10 minutes at 232°C and 3350 psi at 232°C after 8000 hours at 232°C in air.<sup>23</sup> TSS exhibited no creep under a load of 1000 psi at 232°C for 60 days. Sandwich specimens (14 in. × 14 in.) using Ti face sheets and PI and Ti core gave the properties in Table 4. In addition, climbing drum peel specimens from

**Table 3. Glass Transition Temperatures of Polyphenylquinoxalines.<sup>20</sup>**

$\left[ \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 - \text{Y} - \text{C}_6\text{H}_4 \\ \diagdown \quad \diagup \\ \text{N} \end{array} \begin{array}{c} \text{Ar} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \\ \diagdown \quad \diagup \\ \text{N} \end{array} \right]_n$			
<i>Y</i>	<i>Ar</i>	$\eta_{inh}$ , dl/g	$T_g$ , °C
—		2.2	370
—		1.3	318
—		1.2	290
—O—		1.9	279
—CO—		2.3	288
—SO <sub>2</sub> —		1.4	324

Ti/Ti panels gave strength at 25°C of 70 in.-lb/3 in. width. The various PPQ adhesive specimens were fabricated from low volatile

content tape (<0.5%, 112 E-glass) in an autoclave with the temperature starting at 25°C and increasing to 400°C under 50–100 psi dur-

**Table 4. Adhesive Properties of PPQ Sandwich Specimens.**

Test Condition	Peel Strength, in.-lb/3 in. width		Flatwise Tensile Strength, psi	
	Ti Core	PI Core	Ti Core	PI Core
25°C	28	34	800	950
232°C after 10 min at 232°C	—	—	750	825

ing  $\sim 1$  hour and maintaining at  $400^{\circ}\text{C}$  under 50–100 psi for 0.5 hour.

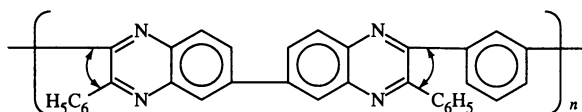
More recent work with the PPQ in Eq. (3) has involved chromic acid and phosphoric acid anodized Ti surface treatments, which result in better moisture resistance but less thermal resistance than the surface from phosphate fluoride treatment. Chromic acid anodized Ti TSS provided strengths of 5000 psi at  $25^{\circ}\text{C}$  (cohesive failure), 2,000 psi at  $232^{\circ}\text{C}$  after 5,000 hours at  $232^{\circ}\text{C}$  in air (mixed failure) and low strengths at  $232^{\circ}\text{C}$  after 10,000 hours at  $232^{\circ}\text{C}$  in air (100% adhesive failure).<sup>24</sup> An anodized Ti surface degrades when bonding temperatures approaching  $370^{\circ}\text{C}$  are employed. This may have been one of the factors which caused lower strengths at  $232^{\circ}\text{C}$  after aging.

This recent work<sup>24</sup> also showed that stressed anodized Ti wedge opening specimens of the PPQ in Eq. (3) exhibited excellent resistance to hydraulic fluid (Skydrol), moisture (95% relative humidity at  $60^{\circ}\text{C}$ ) and crack propagation at  $232^{\circ}\text{C}$ . To demonstrate the processability of this PPQ, a 4 ft  $\times$  4 ft Ti bonded panel (half metal-to-metal and half sandwich structure using PI core) was fabricated. The bonded structure had a dense bondline as evidenced by ultrasonic scanning (C-scan) and high strength as demonstrated by testing specimens taken from various areas of the panel.

A PPQ of structure 4 with a  $T_g$  of  $318^{\circ}\text{C}$  was evaluated for joining Ti to composite and com-

than at  $25^{\circ}\text{C}$  because TSS undergo a peel moment during testing and brittle materials often exhibit more toughness at elevated temperatures. The 710 PI matrix is brittle at  $25^{\circ}\text{C}$  due to crosslinking but becomes softer, more thermoplastic-like, and able to accommodate a higher peel stress at elevated temperatures. This is in contrast to the NR150B2 matrix, which is a tough, high  $T_g$ , thermoplastic PI; the NR150B2 specimens provided high strengths under all test conditions. A strength of 2800 psi at  $316^{\circ}\text{C}$  for the NR150B2 HTS/NR150B2 HTS specimens was observed, whereas pronounced thermoplastic failure occurred in the Ti/Ti specimens at  $316^{\circ}\text{C}$  ( $T_g$  of the PPQ was  $318^{\circ}\text{C}$ ). However when the NR150B2 HTS/NR150B2 HTS specimens were placed under a load of 1500 psi at  $316^{\circ}\text{C}$ , thermoplastic failure in the bondline occurred in  $\sim 15$  minutes.

The effect of a 3-day water boil on the strength of adhesive specimens of the PPQ in structure 4 is summarized in Table 6. The phosphate fluoride surface treatment is sensitive to moisture and this is reflected in low strengths after 3-day water boil. The anodized surface is significantly more resistant to moisture than the phosphate fluoride surface, but the PPQ apparently absorbed water after the 3-day water boil and became plasticized, exhibiting what appeared to be thermoplastic failure at  $288^{\circ}\text{C}$ . This was surprising since PPQs gen-



4

posite to composite for high temperature applications.<sup>22</sup> The molecular weight of the PPQ was controlled to obtain the best combination of processability and adhesive strength. The adhesive properties of Ti/Ti, Ti/composite, and composite/composite TSS are summarized in Table 5. The strengths of the 710 HTS (PI composite) specimens were higher at  $288^{\circ}\text{C}$

erally have relatively low moisture pickup. The composite specimens exhibit good strengths after a 3-day water boil.

PPQs have undergone evaluation by various organizations and have exhibited promise for use as high temperature structural adhesives. A limiting factor in their development has been

**Table 5. PPQ Adhesive Properties.<sup>22,a</sup>**

Specimen	Tensile Shear Strength, psi				
	25°C	288°C	288°C after 300 hr at 288°C	316°C	316°C after 300 hr at 316°C
Ti/Ti <sup>b</sup>	440	2500	2400	300 <sup>c</sup>	500 <sup>c</sup>
Ti/710HTS <sup>c,f</sup>	2000	3100	2800	1600	1900
710HTS/710HTS <sup>f</sup>	3000	4200	2600	3000	2100
NR150B2HTS/ <sup>d</sup>	6000	3700	3300	2800	2500
NR150B2HT <sup>f</sup>					

PPQ with inherent viscosity of 0.61 dL/g and  $T_g = 318^\circ\text{C}$ ; for Ti/Ti, 112 E-glass with A-1100 finish, tape dried to ~4% volatile content; other panels, unsupported PPQ film had ~4% volatiles

<sup>a</sup>Bonding conditions: under 200 psi, 25°C to 400°C during ~0.5 hr, held at 400°C for 20 min, cooled to 260°C, removed from press.

<sup>b</sup>Surface treatment: Ti(6A1-4V), phosphate fluoride.

<sup>c</sup>Unidirectional composite of Monsanto's polyimide composite matrix designated Skybond 710 and Hercules high tensile strength carbon fiber reinforcement, composite surface treatment was mild abrasion.

<sup>d</sup>Unidirectional composite of DuPont's polyimide composite matrix designated NR150B2 and Hercules high tensile strength carbon fiber reinforcement.

<sup>e</sup>Thermoplastic failure.

<sup>f</sup>All composite adherends exhibited shear-type failure in the composite.

commercial unavailability, which is associated with cost. Several companies have considered the PPQ in Eq. (2) as a potential product, but the problems associated primarily with the tetraamine, a suspected carcinogen, the synthesis of the bisbenzil, and a questionable marketplace have discouraged them. An area that merits further investigation with PPQ is the use of amorphous boron as a filler in conjunction with high temperature curing (e.g.,  $>400^\circ\text{C}$ ). This combination provided excellent high temperature adhesive properties for a PQ but has not been evaluated with a PPQ.

### Crosslinked Phenylquinoxaline Polymers

Crosslinked phenylquinoxaline polymers evaluated as adhesives are primarily of two differ-

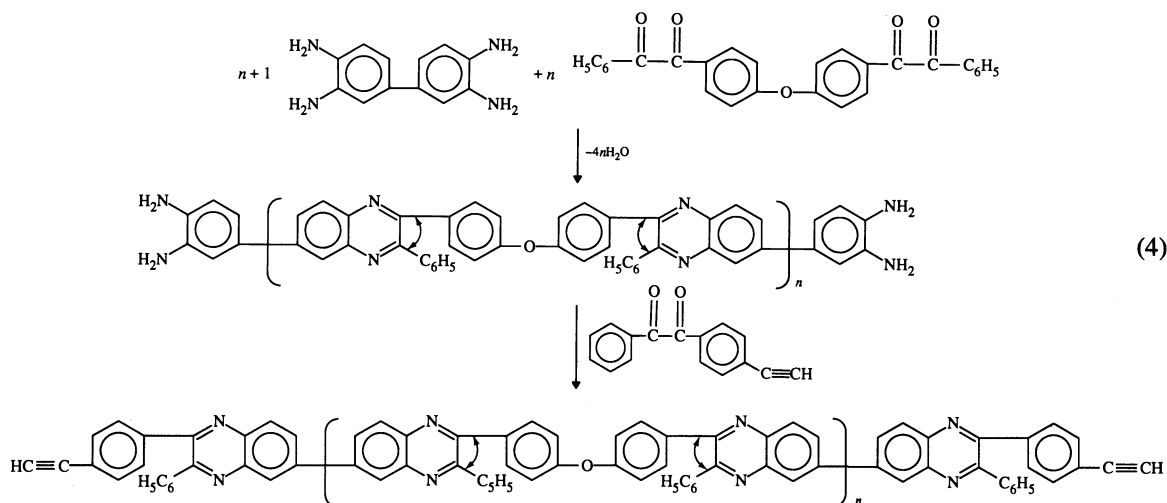
ent types. One type consists of phenylquinoxaline oligomers terminated with reactive groups, primarily acetylenic groups. The other type is a linear PPQ containing pendent acetylenic groups. Upon heating, the acetylenic groups in both types of materials undergo a complex reaction that causes branching and crosslinking. As a result, the  $T_g$ s for these types of cured resins are higher than those of the corresponding linear polymers.

The initial synthesis of acetylenic terminated phenylquinoxaline oligomers was reported in 1975.<sup>25</sup> An alternate synthesis<sup>26</sup> reported in 1976 involved endcapping *o*-diamino-terminated phenylquinoxaline oligomers with 4-(4-ethynylphenoxy)benzil to yield acetylene-terminated phenylquinoxaline oligomers (ATPQs) as shown in the representative scheme in Eq. (4):

**Table 6. Effect of 3-Day Water Boil on PPQ Adhesive Specimens.<sup>22,a</sup>**

Specimen <sup>a</sup>	Surface Treatment	Tensile Shear Strength, psi		Failure Mode
		25°C	288°C	
Ti/Ti	phosphate fluoride (PF)	< 1000	—	100% adhesive
Ti/Ti	phosphoric acid anodized (A)	3530	730	25°C, 20% adhesive
Ti/710HTS	A/mild abrasion	2750	2620	288°C, thermoplastic
710HTS/710HTS	mild abrasion	2650	2950	composite

<sup>a</sup>Bonding conditions, see Table 5



The main advantage offered by the ATPQ over the linear high molecular weight PPQ was better processability. Generally, small molecules of the same type of material exhibit better flow at lower temperatures than large molecules. In addition, the acetylenic groups react without the evolution of volatiles. One of the problems encountered with many acetylenic terminated heterocyclic oligomers is that the acetylenic group begins to react prior to the formation of a complete melt, thereby inhibiting further flow and wetting. In spite of this, Ti/Ti TSS of the ATPQ in Eq. (4) (where  $n = 2$ ) gave strengths of 4730 psi at 25°C, 1350 psi at 260°C after 500 hours at 260°C and 1525 psi at 316°C.<sup>27</sup> The specimens were fabricated at 316°C under 50 psi for 1 hour. Although the cured ATPQs were less stable under thermooxidative conditions than a comparable linear PPQ, they exhibited improved processability. ATPQs are not commercially available.

In 1981, high molecular weight linear PPQs containing pendent ethynyl and phenylethynyl groups were reported.<sup>29</sup> These polymers were soluble in a variety of chlorinated or phenolic solvents, and solutions thereof could be used to cast film or impregnate a carrier or reinforcement. Upon heating, the ethynyl (acetylenic group) and the phenylethynyl groups react to provide branching and crosslinking. As a result, the cured polymers are insoluble and exhibit high  $T_g$ s. A few of the PPQs containing pendent phenylethynyl groups have been evaluated as adhesives, whereas the PPQs containing pendent ethynyl groups did not exhibit adequate processability for fabrication of high strength adhesive specimens.

The linear PPQ and the cured PPQ containing 10 mole % of pendent phenylethynyl groups, as shown in structure 5, exhibited the tensile shear strengths in Table 7. The effect of crosslinking due to reaction of the pendent

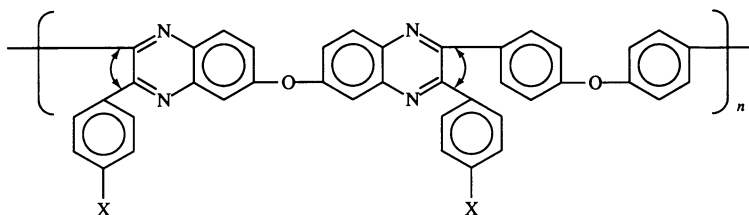
**Table 7. PPQ Ti/Ti Tensile Shear Strength.<sup>30</sup>**

Polymer	$T_g$ , °C	Processing Conditions				Avg. Tensile Shear Strength, psi		
		Final Temp., °C	Pressure, psi	Time, hr	Postcure, hr at Temp., °C	26°C	204°C	232°C
No $\text{C}\equiv\text{C}-\text{C}_6\text{H}_5$	256	316	200	0.5	2 @ 371	4930	2810	2370
10 mole % $\text{C}\equiv\text{C}-\text{C}_6\text{H}_5$	281	329	200	2.0	2 @ 371	4400	3240	3100

phenylethynyl groups is evident in the higher strengths at 204 and 232°C. Another representative PPQ containing pendent phenylethynyl groups which had undergone adhesive evaluation is shown in Eq. (5):

### Imide Polymers

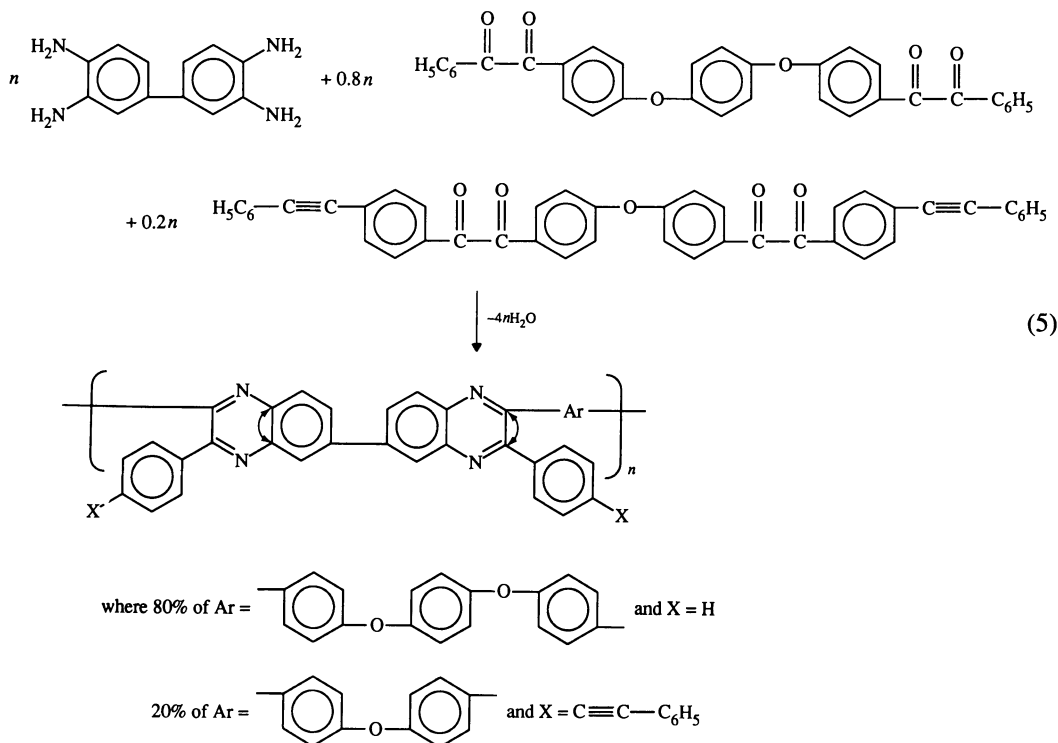
About the time PBI was being developed as a high temperature adhesive, PIs were also receiving attention. The early synthesis of PIs involved the reaction of an aromatic dianhydride



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The Ti/Ti tensile shear strengths as a function of cure conditions are presented in Table 8. The strength at 232°C of 4400 psi for the Al filled specimens is outstanding. PPQs containing pendent phenylethynyl groups are experimental materials and not commercially available.

and an aromatic diamine to form a polyamide acid (amic acid) which was subsequently cyclodehydrated to the PI.<sup>32,33</sup> The cyclodehydration is accomplished thermally when PIs are used as adhesives. Since this early work, several other routes have been devised to synthesize PIs. A representative reaction scheme for PI formation is in Eq. (6).



**Table 8. PPQ Ti/Ti Tensile Shear Strengths.**<sup>31,a</sup>

Polymer ( $T_g$ , °C)	Process Conditions	Tensile Shear Strength, psi		
		25°C	232°C	316°C <sup>b</sup>
No $C\equiv C-C_6H_5$ (255)	RT to 343°C, 100 psi, 0.5 hr hold	5600	3800	Thermoplastic
20% $C\equiv C-C_6H_5$ (262)	RT to 343°C, 300 psi, 0.5 hr hold	4430	3240	840
20% $C\equiv C-C_6H_5$ (278)	RT to 343°C, 300 psi, 4 hr hold	2600	2800	1240
20% $C\equiv C-C_6H_5$ (283)	RT to 343°C, 300 psi, 0.5 hr hold; 16 hr @ 316°C	2300	3180	1350
20% $C\equiv C-C_6H_5$ (272)	RT to 343°C, 300 psi, 0.5 hr hold; 16 hr @ 316°C no glass carrier, 30 phr MD105 Al	4670	4400	1170

<sup>a</sup>Ti surface treatment, 10 V chromic acid anodized, 112 glass with A-1100 finish, no filler.

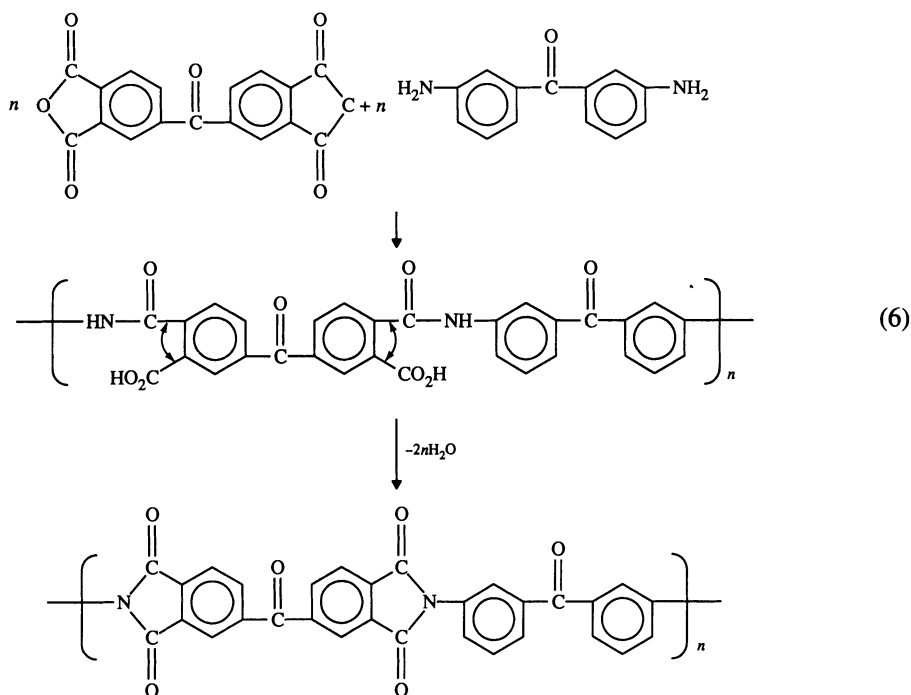
<sup>b</sup>Predominantly thermoplastic failure.

where 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) is reacted with 3,3'-diaminobenzophenone to form a polyamide acid which is converted to the PI. The  $T_g$ s for a series of PIs are presented in Table 9. Several reviews on PIs are available.<sup>35-38</sup>

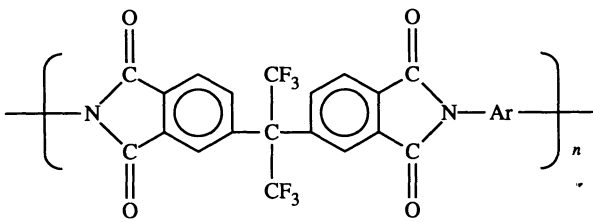
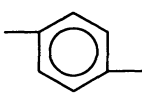
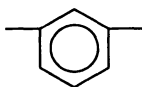
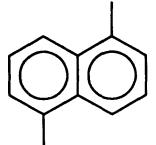
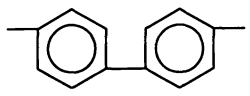
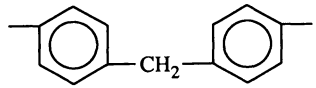
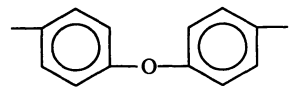
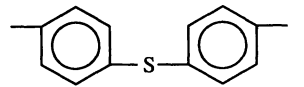
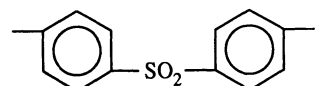
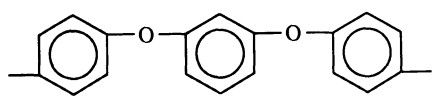
Most of the early PIs were insoluble and many relatively intractable. The soluble polyamide acid was used as the processable precursor to PI. The polyamide acid is unstable at ambient temperature and slowly degrades due to hydrolysis from water evolved during imi-

dization (even at ambient temperature).<sup>39</sup> Another problem with the use of the polyamide acid form in adhesives is the evolution of water during thermal conversion to the PI. This volatile evolution results in processing problems, especially in large area bonding, and in lower mechanical properties primarily due to porosity in the bondline. In spite of these problems, PI adhesives in the form of polyamide acids are currently commercially available.

Many polyimides have been evaluated as ad-



**Table 9. Glass Transition Temperatures of Polyimides.<sup>34</sup>**

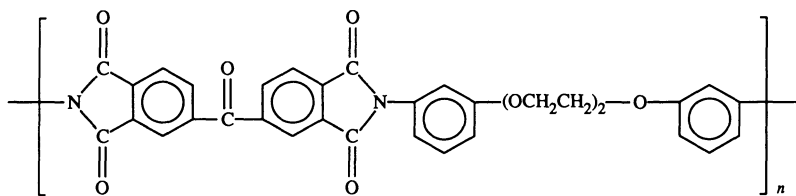
		
<i>Ar</i>	$\eta_{inh}, dL/g$	$T_g, ^\circ C$
	0.35	326
	0.41	297
	0.64	365
	0.40	337
	0.38	291
	0.46	285
	0.35	283
	0.31	336
	0.35	229

hesives using the polyamide acid and PI forms. To circumvent the volatile problem, the PI from the polycondensation of BTDA and 1,3-dia-

minobenzene was processed into adhesive specimens as a thermoplastic at pressures of ~200 psi and temperatures of ~400°C.<sup>40</sup> Ti







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Many other high temperature PIs have also been evaluated as adhesives but their Ti TSS strengths were less than those reported for LARC-TPI. The processing conditions for these other PIs were generally comparable to or higher than those used for LARC-TPI. All high temperature PIs evaluated as adhesives have common problems which are volatile evolution from the polyamide acid and in some cases the use of a mixture of monomers or high melt viscosity of the PI. The use of the polyamide acid or monomer mixture is not recommended for the fabrication of high quality, large area metal-to-metal or metal-to-honeycomb bonded components. The volatiles are difficult to remove to obtain a void-free bondline and high strength bond. The PI form necessitates the use of relatively high pressure, which can be used for the fabrication of large area metal-

to-metal bonds and in some cases, even composite-to-composite bonds. However, the melt viscosity is too high to permit proper filleting around the cells in sandwich structure and in addition, the high pressure will crush the core.

Recent adhesive work with PI has been directed towards improving the processability while retaining high temperature properties. One representative example involves a blend of a low molecular weight acetylene terminated imide with a high molecular weight PI.<sup>51</sup> The blend has a relatively low melt viscosity at moderate temperatures. Upon heating under low pressure (50 psi), the acetylenic groups react with no volatile evolution in the presence of the high molecular weight PI to provide a semi-interpenetrating polymer network (SIPN). The reactive low molecular weight oligomer improves the processability of the high molec-

**Table 10. Properties of PI of Structure 6.<sup>49</sup>**

Glass transition temperature: 222°C Crystalline melt temperature: 350°C Solvent resistance: excellent		
Thin Film Properties		
Test temperature, °C	25	177
Tensile strength, psi	22,000	14.2
Tensile modulus, psi	630,000	540,000
Elongation, %	8.3	21.1
Fracture toughness ( $G_{Ic}$ ) at 25°C: 37.8 in.-lb/in. <sup>2</sup>		
Adhesive Properties <sup>a</sup>		
Test Condition	Ti/Ti Tensile Shear Strength, psi	Failure
25°C	6250	> 95% cohesive
25°C after 1000 hr @ 232°C	7120	~ 100% cohesive
25°C after 72 hr water boil	5140	~ 90% cohesive
177°C	4150	> 95% cohesive
232°C	880	~ 95% adhesive
232°C after 1000 hr @ 232°C	2740	~ 50% cohesive
232°C after 5 hr @ 300°C	2800	~ 80% cohesive
232°C after 100 hr @ 316°C	3670	> 95% cohesive

<sup>a</sup>Pasa Jell 107 surface treatment; bonding conditions, 400°C, 1000 psi, 15 minutes.

ular weight PI while the molecular weight PI enhances the toughness of the cured resin from the low molecular weight reactive oligomer. Ti TSS gave strengths of 3300 psi at 25°C, 2800 psi at 232°C and 3000 psi at 232°C after 1000 hours at 232°C.<sup>51</sup> Other combinations are being evaluated for potential use in high temperature adhesive and composite applications.

A few PIs are commercially available in adhesive form as the polyamide acid with the most popular being FM 34B -18.<sup>52</sup> Another is the polyamide acid form of LARC-TPI which can be formulated and used to prepare adhesive tape.<sup>53</sup> Several other polyimides, as discussed in a review on aromatic polyimide adhesives and bonding agents,<sup>54</sup> are also available.

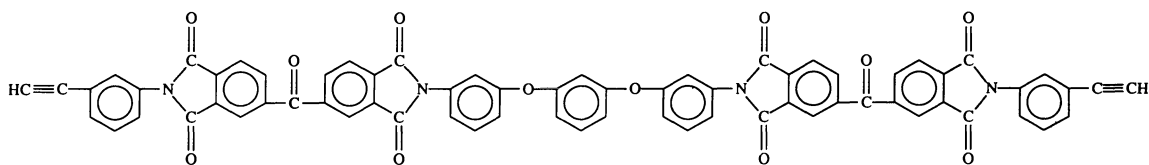
### Addition Polyimides

Two types of reactive groups, ethynyl and norbornene (Nadic), have been placed on the ends of imide oligomers in an attempt to develop more processable high temperature PI adhesives. The thermal reaction of the ethynyl groups occurs without the evolution of volatiles, whereas the thermal reaction of the norbornene group may involve the release of a small amount of cyclopentadiene from the reverse Diels-Alder reaction (depending on con-

The preferred method to convert the ethynyl terminated amide acid to the corresponding imide is chemically (e.g., acetic anhydride and an organic base). Under chemical conversion, the ethynyl group remains unreacted.

One of the major problems with ethynyl terminated oligomers with high melt or softening temperatures is that the ethynyl groups begin to react before the oligomer softens or melts. As the ethynyl group reacts, the temperature for softening or melting of the oligomer is increased. Therefore, certain ethynyl terminated oligomers such as some imides cannot provide adequate wetting of the substrate, which is required to form a strong bond. Obviously, heating rate is important with reactive oligomers. A fast heating rate is desirable to achieve adequate flow and wetting but impractical from a manufacturing standpoint. Autoclaves and large presses heat slowly whereas preheated matched metal tooling can heat more rapidly.

The ethynyl terminated imide oligomer work was initially reported in 1974.<sup>55,56</sup> Neat resin<sup>57,58</sup> and composite<sup>57-59</sup> properties for cured acetylene terminated imide oligomers have been reported. These materials were initially designated HR-600 and later Thermid®-600 (60). The ethynyl terminated imide oligomer in structure 8 is representative of this class



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ditions). Nadic end-capped amide acid oligomers can be converted predominantly to the nadic end-capped imide oligomer under thermal conditions, generally at temperatures < 200°C. The thermally induced reaction of the nadic group proceeds at a slow rate at temperatures < 200°C and at a fast rate at temperatures of > 275°C. However, the thermal conversion of the ethynyl end-capped amide acid oligomer to imide is more difficult since the ethynyl group undergoes substantial reaction in the temperature range of 150–200°C.

of materials. Ti/Ti TSS of the cured material of structure 7 provides strengths of 3200 psi at 25°C, 1900 psi at 232°C after 1000 hours at 232°C, and 1200 psi at 260°C after 1000 hours at 260°C.<sup>61</sup> Hydroquinone has been used to retard the thermal reaction of the ethynyl group and thereby improve the processability by increasing the gel time.<sup>62</sup> Strengths of Ti/Ti TSS of 3800 psi at 25°C, 2100 psi at 288°C, and 2550 psi at 288°C after 500 hours at 288°C were reported.<sup>62</sup> These bonds were fabricated in a press starting at 25°C under 50 psi, in-

creasing the temperature to 316°C during 1.5 hours and holding at 316°C for 1.5 hours. The bonds were subsequently postcured unrestrained for 4 hours at 343°C.

Other work to improve the processability of reactive imide-type oligomers has involved the preparation of ethynyl terminated isoimide oligomers. The ethynyl terminated amide acid oligomer is normally treated with a chemical cyclodehydrating agent such as trifluoroacetic anhydride or dicyclohexylcarbodiimide to form the corresponding isoimide oligomer. The ethynyl terminated isoimide oligomer exhibits better solubility and processability than the ethynyl terminated imide oligomer.<sup>63</sup> The isoimide rearranges to the imide during the thermal curing process, generally in the temperature range of about 300–350°C.<sup>64</sup> The strength of Ti/Ti TSS of cured ethynyl terminated isoimide oligomers is about the same as that reported for HR-600. Various forms of ethynyl terminated amide acid, imide and isoimide oligomers are commercially available.<sup>60</sup>

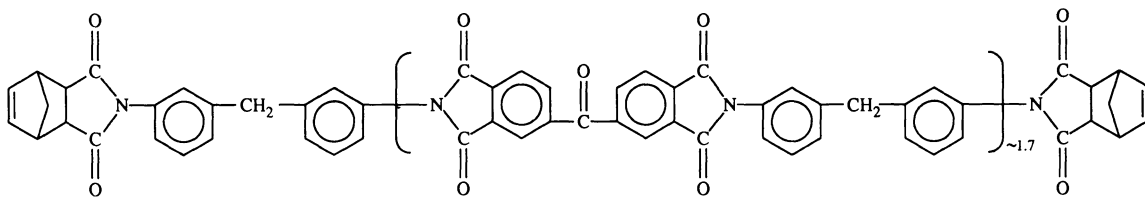
Nadic terminated imide oligomers were first reported in 1970,<sup>65</sup> and led to the development of PMR-15 (PMR means in situ polymerization of monomeric reactants to yield an oligomer with number average molecular weight,  $M_n$ , of about 1500 g/mole).<sup>66</sup> PMR-15 is used as a matrix resin in composites for hot applications such as components in jet engines. The first report on the evaluation of Nadic terminated imide oligomers as adhesives was in 1979,<sup>67</sup> using a material called LARC-13 ( $M_n = \sim 1300$  g/mole, structure 9). This material was processed under mild pressures (50 psi) to a final cure temperature of 329°C followed by an unrestrained postcure at 343°C. Ti/Ti, Ti/composite and composite/composite TSS were fabricated and tested. The strengths of Ti/Ti TSS were 3300 psi at 25°C and 2800 psi at 260°C.<sup>67</sup> Composite to composite TSS gave

strengths as high as 5000 psi at 25°C and 2200 psi at 316°C.<sup>67</sup> A beveled honeycomb panel (about 2 ft  $\times$  3 ft) using PI composite skins and LARC-13 as the adhesive was successfully fabricated and performed well in static tests at 25 and 260°C.<sup>67</sup> LARC-13 is not commercially available because of the unavailability and cost of the diamine, 3,3'-diaminodiphenyl methane, used to prepare the oligomer. A PMR-15 type adhesive (BXR10314-151C) is commercially available.<sup>52</sup>

### Arylene Ether Polymers

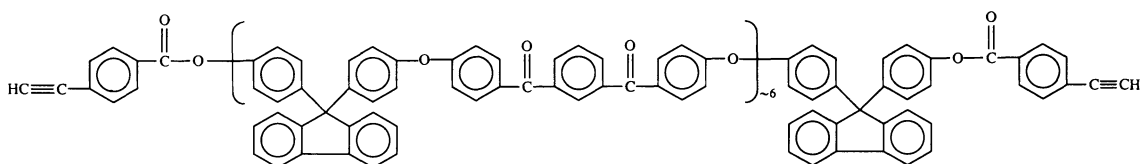
Several polyarylene ethers such as UDEL® (polysulfone,  $T_g \sim 190^\circ\text{C}$ ),<sup>68</sup> RADEL® (polyphenylsulfone,  $T_g \sim 220^\circ\text{C}$ ),<sup>68</sup> Kadel-II® (polyketone,  $T_g \sim 160^\circ\text{C}$ ,  $T_m \sim 340^\circ\text{C}$ ),<sup>68</sup> Victrex® PES (polyethersulfone,  $T_g \sim 220^\circ\text{C}$ ),<sup>65</sup> and Victrex® PEEK (polyetheretherketone,  $T_g \sim 143^\circ\text{C}$ ,  $T_m \sim 343^\circ\text{C}$ )<sup>65</sup> are commercially available high performance engineering thermoplastics. However, although the thermooxidative stability of these materials is excellent, they cannot be classified as high temperature adhesives because their  $T_g$  dictates their use temperature. None of these polyarylene ethers, even in filled form, exhibit good retention of mechanical properties at 232°C under stress for long term. Research is underway to develop new polyarylene ethers with higher use temperature. For example, experimental quantities of new versions of PEEK (e.g., HTX,  $T_g = 205^\circ\text{C}$ ,  $T_m = 386^\circ\text{C}$ ; different chemical structure) with higher  $T_g$ s and accordingly higher  $T_m$ s are being sampled to various organizations.

In the case of PEEK, a semicrystalline polymer, Ti/Ti (chromic acid anodized) TSS gave strengths of 6370 psi at 25°C, 2590 psi at 177°C and 1770 psi at 232°C.<sup>70</sup> The crystalline regions of the polymer carry the load at temperatures above the  $T_g$ . However, under a



load of 1000 psi at 177°C, creep was observed in the TSS. Perhaps a higher degree of crystallinity could have prevented or reduced the creep behavior. These TSS were fabricated at ~380°C under 200 psi for 0.5 hour. As men-

As part of a study<sup>74</sup> on polyarylene ethers, several polymers with high  $T_g$ s as presented in Table 11 were prepared. The first polymer in Table 11 and an ethynyl terminated oligomer shown in structure **10** were evaluated as adhe-



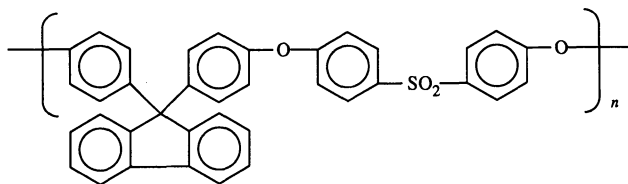
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tioned previously, the high processing temperatures have been considered one of the detriments to the acceptance of high temperature thermoplastics as structural resins. This may be a misconception, since high temperatures are widely used in many manufacturing steps such as ceramic processing and metal forming. Similar but milder conditions could be used to fabricate bonded structure from tough high temperature polymers.

An arylene ether polymer (Polymer 360 or Astrel 360) which was commercially available<sup>71</sup> in the 1970s has also undergone preliminary evaluation as an adhesive.<sup>72</sup> This polymer composed of biphenyl and phenyl units connected by oxygen and sulfone units has a  $T_g$  of

232°C. However, the results show the advantageous effect of a small amount of crosslinking in improving the elevated temperature strength and resistance to hydraulic fluid.

Another arylene ether polymer in structure **11** provided Ti/Ti (chromic acid anodized) TSS

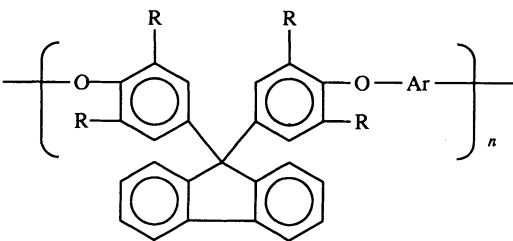
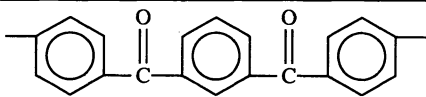
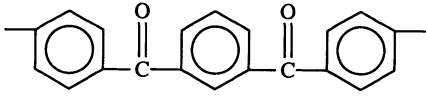
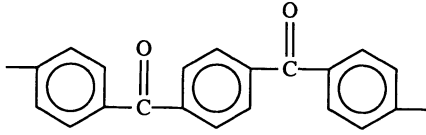
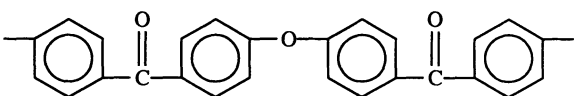
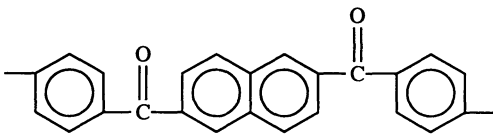
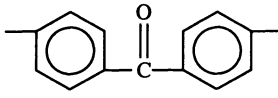
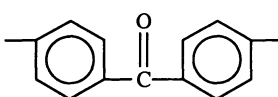
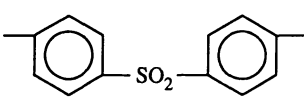
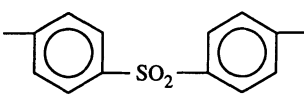


11

~290°C. Because of the high  $T_g$  and high melt viscosity, a temperature of 400°C and a pressure of 200 psi were required to fabricate TSS. On Ti substrate, strengths of 4600 psi at 25°C, 3700 psi at 232°C and 3170 psi at 260°C were obtained.<sup>73</sup> No results on the effect of exposure to solvents were reported. Since this polyarylene ether is amorphous, it would likely undergo attack by solvents such as hydraulic fluid or paint stripper.

with strengths of 3620 psi at -54°C, 3380 psi at 25°C, 3070 and 3210 psi at 177°C initially and after 1000 hours at 177°C respectively and 2440 and 2590 psi at 232°C initially and after 1000 hours at 232°C, respectively.<sup>76</sup> Climbing drum Ti/Ti peel specimens gave 25°C values of 16.3 in.-lb/in. width. The Ti/Ti TSS were severely attacked while under stress in the presence of hydraulic fluid (Skydrol). The final bonding conditions using tape (112 E-glass with

Table 11. Properties of Polyarylene Ethers.<sup>74</sup>

				
Ar	R	$\eta_{inh}$ , dL/g	$M_n$ , g/mole	$T_g$ , °C
	H	0.95	28,300	223
	CH <sub>3</sub>	1.24	—	257
	H	1.7	39,900	243
	H	Insoluble	—	231
	H	1.29	—	252
	H	1.00	34,000	252
	CH <sub>3</sub>	0.37	—	294
	H	0.67	26,700	280
	CH <sub>3</sub>	0.64	—	310

**Table 12. Ti/Ti Tensile Shear Strength of Polyarylene Ethers.<sup>77,a</sup>**

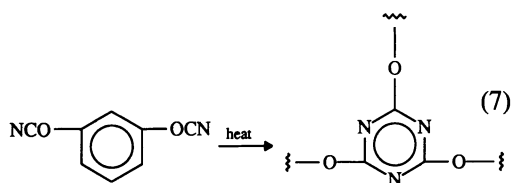
Test Condition	Tensile Shear Strength, psi (Failure Mode)	
	Linear Polyarylene Ether (PAE)	Ethynyl Terminated PAE ( $M_n \sim 4000$ g/mole)
25°C	5450 (coh)	4300 (mixed)
93°C	4550 (coh)	4200 (mixed)
150°C	3500 (coh)	3800 (mixed)
25°C after 72 hr soak in hydraulic fluid	1500 (~ 50% coh)	4400 (mixed)

<sup>a</sup>Pasa-Jell 107 surface treatment, RT to 260°C under 50 psi, held at 260°C 0.5 hr.

A1100 finish) containing 0.5% volatile content were 343°C under 100 psi for 1 hour. The time at temperature could be reduced to a few minutes since this polymer is a thermoplastic (no chemical reaction during the bonding cycle). No polyarylene ethers are currently commercially available that can be classified as high temperature adhesives.

### Other Polymers

Although many organizations have been involved in high temperature adhesive development for captive use and as a service to their customers, most of this information is proprietary and the remainder is seldom published. An example of a promising adhesive with the potential for high temperature application is the cured resin from 1,3-dicyanatobenzene (resorcinol dicyanate) as shown in Eq. (7):



Preliminary adhesive properties are presented in Table 13. Double lap TSS were used with stainless steel and Ti adherends whereas single lap specimens were used with aluminum adherends. The peel moment encountered in testing TSS is essentially eliminated in double lap specimens. Therefore, brittle materials generally exhibit significantly higher strength in double lap specimens than in single lap specimens. As shown in Table 13, the strength of TSS at 232°C after 233 hours at 232°C was excellent.

No aging and subsequent testing were performed beyond those in Table 13. Resorcinol dicyanate is one of many examples where excellent potential was demonstrated but no further results are available. Problems such as availability, toxicity, moisture and solvent resistance, low shelf life, processability, etc. often discourage further adhesive development. Resorcinol dicyanate is unavailable but a few other dicyanates are commercially available.<sup>78</sup> No adhesive properties have been reported on these dicyanates. The adhesive work on resorcinol dicyanate is representative of company funded research that is not readily available to the public.

In addition to the high temperature polymers discussed as adhesives, many other high temperature polymers have been reported. However, no adhesive work on these other polymers have been reported. Information on the chemistry and properties of these polymers can be found in various sources (e.g., Refs. 79–81). Adhesive work on some of the more promising polymers such as the polyquinolines, polyquinazolidinediones and highly phenylated polyimides may not have been performed because of the problems (e.g., high melt viscosity or volatile evolution) which have plagued other high temperature polymers.

### Concluding Remarks

Although several polymers have shown potential for use as high temperature adhesives, they exhibit certain shortcomings such as limited flow which necessitates the use of high temperatures and pressures, volatile evolution which leads to processing problems and fre-

**Table 13. Tensile Shear Strength of Resorcinol Dicyanate Resin.<sup>77,a</sup>**

<i>Adherend (Surface Treatment)</i>	<i>Test Conditions</i>	<i>Strength, psi</i>
2024 TS Al <sup>b</sup> (Dichromate etch)	26°C	5940
	216°C	5490
	216°C after 233 hr at 232°C	4470
17-7 PH SS <sup>c</sup> (Phosphate etch)	26°C	5720
	232°C	5680
	232°C after 233 hr at 232°C	5560
8-1-1 Ti <sup>c</sup> (Phosphate fluoride etch)	26	5260
	177	5340

<sup>a</sup>Cured 1.5 hr at 177°C, 0.25 hr at 232°C, 1 hr at 288°C under 20 psi.

<sup>b</sup>Single lap specimens.

<sup>c</sup>Double lap specimens.

quently low strength, and high cost which discourages their use except in specialty high performance applications. To improve the state of high temperature adhesives, research should be directed towards the following important items.

- Better processability from volatileless systems.
- In situ polymerization route to high  $T_g$ , solvent resistant, tough polymers without volatile evolution.
- More durable higher temperature performing polymers.
- Better surface preparation of adherends, particularly Ti and composites.
- Better quality control of surface treatment process.
- Innovative low cost process to prepare adhesive tapes and fabricate bonded structures.
- Better nondestructive evaluation tests.
- Lower cost high temperature adhesives.

As mentioned previously in this article, a single adhesive system cannot perform in all the different applications because the requirements vary significantly. As a result, high temperature adhesive systems are often developed for a particular application. High temperature adhesive development during the last two decades has been sporadic primarily because of a questionable market. New markets are developing in the military arena and a new thrust in

high speed commercial transports (formerly called supersonic transports) may occur. These two areas offer the potential of a sizable market for high temperature structural adhesives. In addition, as improvements in processability and performance are made in higher temperature adhesives, larger markets will develop which will lower the cost and stimulate the use of high temperature adhesives in other applications.

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# Silicone Adhesive Sealants and Abhesives

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Silicones are synthetic polymeric materials that possess an extraordinarily wide range of physical properties. They can be low- or high-viscosity liquids, solid resins, or vulcanizable gums. As a class of substances, silicones are characteristically very resistant to extremes of temperature, to ultraviolet and infrared radiation, and to oxidative degradation. They display an unusual combination of organic and inorganic chemical properties that are due to their unique molecular structure of alternating silicon and oxygen atoms; this polysiloxane chemical structure is common to all silicones.

These versatile polymers can be compounded with other chemicals and fillers into an enormous variety of products that serve in a multitude of applications. This chapter will describe the product types, chemistry, and applications of only one major class of silicone products, the adhesive sealants. In addition, the class of silicone *abhesive* products will be described and discussed; these materials are employed where “release” characteristics are desired, rather than adhesion.

## ROOM TEMPERATURE VULCANIZING SYSTEMS

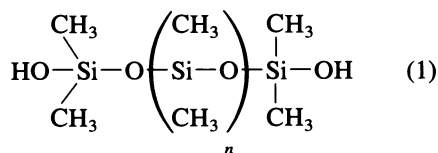
The room-temperature-vulcanizing (RTV) concept is centered on the development of a cross-

linked elastomer from relatively low molecular weight linear polymers by means of a chemical reaction that forms these crosslinks and extends polymer chain length simultaneously. The reaction is initiated at the time that the product is put into use. The principal advantage of this concept is that low viscosity polymers can be employed in the formulation, resulting in products that can be poured, spread, tooled, or otherwise applied very easily with little or no molding equipment and without the need for external energy input in most cases.

These materials are stable in storage for many months or years either as one-package or as two-package systems. In general, many two-package systems tend to have longer shelf age capabilities because the chemically reactive components can be separated until the time of use. However, some one-component products, such as the acetoxym sealants, also have excellent shelf stability and remain useful for up to three or four years after manufacture.

## Polymers

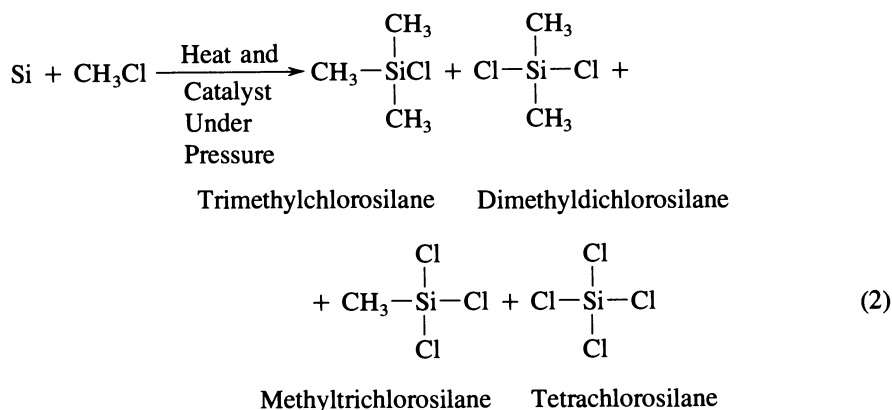
The fundamental component of most silicone sealants is the polymeric siloxane referred to earlier, most often a silanol-terminated poly(dimethylsiloxane):



where  $n$  is about 300–1600.

These polymers are made by an equilibration process from other siloxanes as described below, and typically range in viscosity from about 2,000 cps to 150,000 cps.

The industrial manufacture of siloxanes has its beginnings with pure silicon, which is pulverized and allowed to react with methyl chloride<sup>1</sup> in a pressurized fluid bed reactor in the presence of a copper catalyst. Under carefully controlled conditions, this reaction yields a mixture of methylchlorosilanes in which dimethyldichlorosilane predominates:



After separation and purification by distillation, the difunctional compound dimethyl dichlorosilane is then allowed to react with water to form a hydrolyzate, which is a mixture of cyclic and linear polydimethylsiloxanes. The linear components are low-molecular weight hydroxyl (silanol) terminated polymers.

This mixture can be condensed and equilibrated by a number of different catalysts, or the cyclic siloxanes can be removed and polymerized separately. Catalysts for these equilibration reactions can be basic, such as the hydroxides of lithium,<sup>2</sup> sodium,<sup>2</sup> potassium,<sup>2</sup> and cesium,<sup>3</sup> and potassium amide.<sup>4</sup> Some acidic catalyst are sulfuric<sup>5</sup> and ethylsulfuric,<sup>6</sup> chlorosulfonic,<sup>7</sup> phosphoric,<sup>8</sup> pyrophos-

phoric,<sup>9</sup> nitric,<sup>9</sup> selenic,<sup>10</sup> boric,<sup>11</sup> and activated Fuller's Earth.<sup>12,13</sup> Most commonly, some form of potassium hydroxide is employed to prepare the higher-molecular-weight polymers, although other catalysts have specialized applications. One final product of this complex process is the silanol-terminated polymer depicted in Eq. (1).

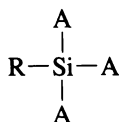
When special properties are needed, other organic functional groups can be substituted for the methyl groups usually present in polysiloxanes; examples are other alkyls, phenyl, cyanoethyl, and trifluoropropyl. For example, a copolymer of dimethyl siloxane with about 5 mole per cent of diphenylsiloxane affords an elastomer that has a much lower brittle point, providing elastomeric properties down to  $-130^\circ\text{F}$  compared with the normal lower limit of  $-65^\circ\text{F}$  for all-dimethyl polymers.

Dimethyl silicone polymers are, because of their relatively low polarities, relatively compatible with hydrocarbons and easily swollen by fuels. Substitution for the methyl functionality by polar cyanoethyl and trifluoropropyl groups imparts significant polarity to these elastomers and makes them resistant to swelling by nonpolar substances; these specialized polymers can be compounded into very useful adhesives and sealants for applications requiring fuel resistance.

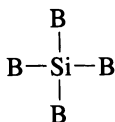
### Crosslinking Systems

In compounding silicone adhesive sealants, an essential ingredient is a crosslinking compo-

nent that reacts with the ends of the polymer chains to simultaneously lengthen them and connect them laterally to form the crosslinked network characteristic of an elastomer. A reactive polyfunctional silane is required, with either three or four reactive groups available to accomplish the necessary crosslinks.<sup>23,24</sup>



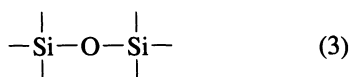
Trifunctional Silane



Tetrafunctional Silane

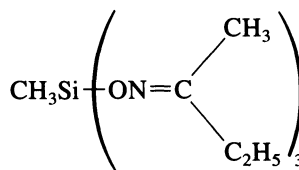
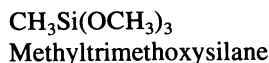
Usually a catalytic agent is included, to facilitate the reaction of the crosslinker with the polymer's silanol (hydroxyl) groups and with water during the crosslinking reaction; some that are commonly used are the tin soaps, alkyl tin carboxylates.<sup>14</sup>

Crosslinking occurs through the formation of new siloxane:

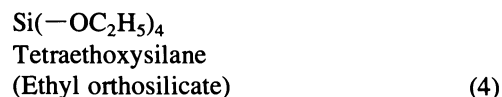
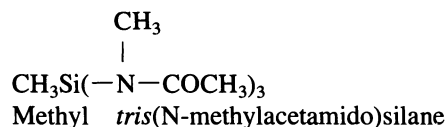
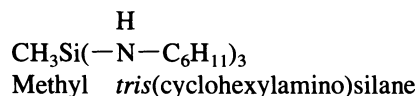


linkages that incorporate the silicon atoms of the crosslinker molecules, with the concomitant release of the crosslinkers' organic functional groups as simple molecules of (preferably volatile) organic species. These low molecular weight organic substances then evaporate from the now-crosslinked polysiloxane which constitutes the cured elastomeric sealant.

Many organosilanes have been employed over the years as crosslinkers; speed of reaction, the nature of the byproducts, and cost have been major factors in the selection of systems for commercialization. Crosslinker silanes that have been employed are those that afford as byproducts alcohols,<sup>14-17</sup> carboxylic acids,<sup>18</sup> amines,<sup>19</sup> ketoximes,<sup>20</sup> aldoximes,<sup>21</sup> and amides.<sup>22</sup> Examples of some of these organosilanes are shown below:



Methyl tris(methylethylketoximino)silane



In the global market, the acetoxo, methoxy, and oxime curing systems are the commercially predominant curing chemistries for one-component sealants. The tetrafunctional ethylorthosilicate is used in two-component formulations.

### Fillers

Many types of fillers have been employed for both one-package and two-package RTV products. They often serve to reinforce the polymer system to achieve significant improvements in strength by means of polymer-filler and filler-filler interactions. High surface area is a prerequisite for any significant reinforcement and the most widely used filler is "fumed silica," formed in high purity by burning silanes in a high-temperature flame. Colorless, translucent compounds are made with fumed silica or its surface-treated versions. Carbon black (used to reinforce organic rubbers) is another high-surface area reinforcing filler effective in silicone polymers, but has an obviously severe limitation of colorability. Silica-filled systems can be

easily made in any desired color with appropriate pigments, and the industry standard is consequently fumed silica.

Many other fillers are found in silicone adhesives, including some that provide very specific enhancements; an example is iron oxide for high-temperature resistance. Zinc oxide, diatomaceous earth, some clays, and glass microballoons are other fillers sometimes used for specific purposes; there are other types of additives to impart special rheological properties, such as thixotropes. Nonreactive silicone oils may also be included in the compound to act as plasticizers in the cured elastomer, and to improve the extrudability of the uncured pastelike sealant. Usually a compound will be composed of several of these ingredients in varying amounts, plus a few percent of pigments. Typical pigments are titanium dioxide, carbon black, and a wide variety of metal oxides, chromates, sulfates, etc. in combinations to provide a range of colors to the finished products. A major nonreinforcing filler often used in sealants is calcium carbonate, either with or without a surface treatment of stearic acid.

## PRODUCTS AND PROPERTIES

The great number of RTV silicone sealants available from a growing group of manufacturers around the world attests to the versatility of the technology, which is in continuous evolution. Silicone adhesive sealants began as exotic high-priced materials in the 1960s; today the pressures of competition and changing costs of materials and processes allow silicones to compete in many markets formerly dominated by lower-cost organic sealants. The characteristics of some typical silicone adhesive sealants will be discussed in the following sections.

### Rheology

Both the one-part and two-part sealants can be made in a range of viscosities and rheologies, from flowable and self-leveling to pastelike thixotropic compositions that will not sag significantly when applied to a vertical surface.

Of particular usefulness to end-users is the relatively small change in viscosity or extrud-

ability that silicone adhesive compounds undergo with extremes in temperature. A typical thixotropic silicone construction sealant can be applied with almost equal ease at room temperature or at subzero conditions, whereas organic sealants typically become extremely viscous at low temperatures. The self-leveling materials are generally in the range of 10,000–50,000 centipoises in viscosity. Thixotropic paste sealants are measured in terms of their extrudability in grams per minute through a fixed orifice at a specified pressure; these values are typically from 100 to 1000 grams per minute through a  $\frac{1}{8}$ " opening at 90 psig.

### Cure Characteristics

It is possible to design a wide variation of cure speed into both the one-part and two-part systems by choice of crosslinking chemistry and by varying the amount and type of catalytic agent. The two-part systems normally contain their own water for hydrolysis of the crosslinker and consequently are capable of deep-section (over  $\frac{1}{2}$  inch) cures, gelling within a few minutes with an active catalyst such as stannous octoate, or in up to several hours with less-active tin soaps such as dibutyl tin dilaurate.

One-part systems are packaged to remain anhydrous until dispensed, and depend upon atmospheric moisture as a reactant to accomplish the crosslinking reaction needed to cure them. The ultimate cure-through of a sealant bead can take from 12 to 72 hours depending upon conditions of temperature and humidity: a  $\frac{1}{8}$ " depth of sealant of one of the faster-curing systems such as the acetox type will cure through at 25°C and 50% relative humidity in about 24 hours. The slower curing systems may need 48–72 hours for the same depth of cure. Exposure of the sealant surface to the atmosphere is required, and conditions of temperature and humidity are major factors affecting the rate at which the sealant will first form a rubbery skin, with subsequent progression of curing throughout the mass of sealant. Higher temperatures and higher humidities accelerate the process. The products are also solventless, and therefore have little shrinkage other than the small loss of cure byproducts.

Package integrity is absolutely essential for moisture-curing one-part sealants, in order to ensure adequate shelf life. Whereas industrial products tend to be used relatively promptly, inventories of adhesive sealants marketed to consumers through commercial distribution often require that the product be usable for several years. Aluminum squeeze tubes in small sizes have been employed for decades successfully. Caulking cartridges evolved in the 1970s from the former spiral-wound foil laminate type to the present plastic caulker which is the industry standard for silicone adhesive sealants for both industrial and consumer packaging. For the industrial user, the sealants are also packaged in plastic and steel pails and drums, with seals that are impervious to moisture.

Two-part RTV elastomers were the earliest room-temperature-vulcanizing silicones and were designed to be primarily potting compounds, not adhesives. One package contained a mixture of silanol-terminated polymers plus fillers and a typical crosslinking system of ethyl silicate and water. This mixture was stable to storage in the absence of catalytic agents, and was caused to crosslink (cure) when a small percentage of a tin soap (part two of the system) was mixed in at the point of use. Within recent years, this basic system has been developed into two-part adhesive sealants of greater chemical complexity with considerable and growing industrial importance.

The second part of the two-part system may now contain the crosslinker in some cases, plus organofunctional silanes that serve as adhesion promoters and catalytic agents. The ratios of the two components are often about ten or more to one, and automatic equipment enables the mixing and dispensing of these products to be done with considerable precision. Two-part sealant technology is employed to make factory-produced insulated glass windows, in which the silicone adhesive sealant provides the secondary perimeter seal for the double-glazed window unit. This type of product is also often used as the structural adhesive that bonds such insulated window units to their supporting frames during the fabrication of factory-glazed window assemblies. Other industrial adhesive

and gasketing applications are developing, as the advantages of this technology have become apparent: relatively rapid, controlled cure rates in thick sections with relatively fast development of adhesion.

### Weathering

Superior resistance to ozone and ultraviolet radiation attack are inherent in the molecular structure of silicone polymers, making unnecessary the use of the additives employed to mitigate this weakness in many organic polymers used for sealants. Silicone elastomeric adhesive sealants perform without cracking and shrinkage in long-term exposure to outdoor weathering in all climates, properties which enhance their usefulness as construction sealants for commercial waterproofing and glazing, and for similar purposes in the consumer market. Their great durability obviates the need for frequent rehabilitative work, more than offsetting their higher initial cost. See Figs. 1 and 2.

### Strength and Elongation Properties

Early two-part RTV silicones were relatively low-strength materials with generally nonreinforcing filler systems. Most of these were used as potting compounds for protection of electrical devices where strength and elastomeric behavior were of little importance.

With advent of one-part adhesive sealants and their development over the past quarter century, much progress has been made in designing products to perform over a range of property profiles to suit the requirements of specific applications. Three general categories may be defined rather arbitrarily based on low, medium, and high strengths; see Table 1. These categories of sealants find use as follows:

- Low strength, low-modulus adhesive sealants are used in building construction waterproofing applications where maximum extensibility is required in expansion joints to accommodate movement. They maintain the seal by stretching easily without losing adhesion to the substrates.



Fig. 1. Shop glazing of insulated glass units.

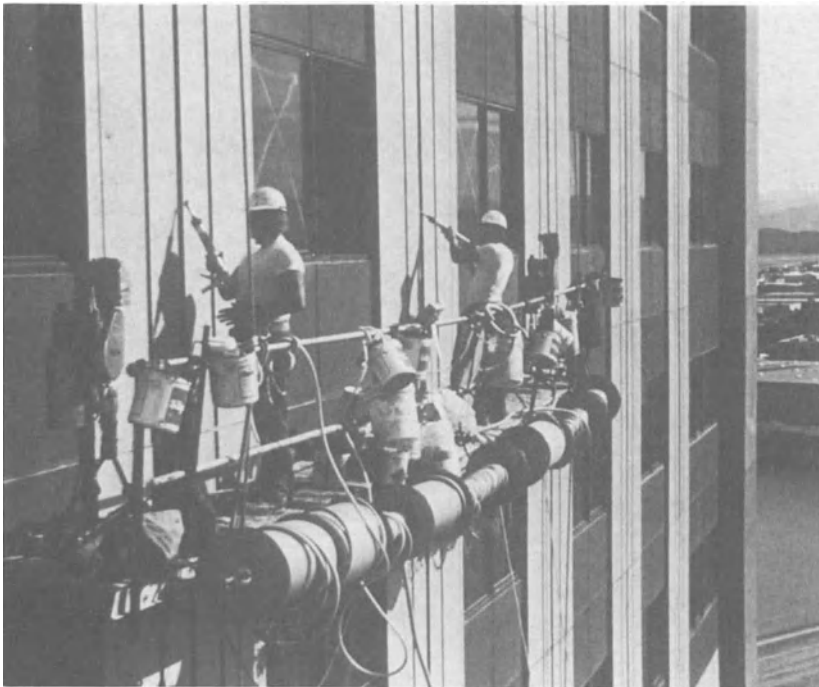


Fig. 2. Waterproofing high-rise building expansion joints.



**Table 1. Strengths of RTV Silicone Adhesive Sealants.**

	<i>Low</i>	<i>Medium</i>	<i>High</i>
Tensile strength, psi	100–200	250–600	600–1200
Elongation, %	100–1200	100–700	300–1000
Hardness, Shore A	10–30	20–60	25–60
Tear strength, lb./in.	10–20	20–80	80–200

- Medium-strength products tend to meet the needs of general purpose construction, industrial and consumer applications. They provide a balance of strength, adhesion, and elastomeric properties for a broad range of uses as both adhesives and as sealants.
- High strength one-part sealants often employ more highly treated fumed silica for reinforcement, and are made with both acetoxo and alkoxy crosslinking systems. These products frequently find applications in the aerospace industry where high-performance adhesives and sealants are required; silicone adhesives are often the most effective materials for bonding heat-cured silicone rubber gaskets to other substrates.

### Thermal Properties

Silicone elastomers are well known for their superior resistance to elevated (and reduced) temperatures, with little or no loss of properties. Again, the siloxane polymer structure is responsible for properties not seen in carbon-based polymers; one reason is the inherent flexibility of the siloxane molecule, and another is its greater resistance to oxidative degradation. When these basic properties are enhanced with appropriate heat-resistant fillers and additives (often iron oxide), a high temperature elastomeric adhesive can be made that will withstand heating in air for up to a year at 400°F without significant property losses. Resistance to even higher temperatures can be achieved for shorter times, as shown in Table 2.

### Electrical Properties

The low polarity of silicone elastomers confers excellent electrical insulation properties to these compounds, enabling them to have great resis-

**Table 2. Thermal Stability of a High Temperature One-Part Sealant.**

<i>Exposure</i>	<i>Original</i>	<i>7 Days</i>	
		<i>@480°F</i>	<i>@600°F</i>
Tensile strength, psi	350	390	420
Elongation, %	400	540	300
Hardness, Shore	33	28	45
Tear strength, lb./in.	50	43	40

tance to high voltage ionization as well as extremely good corona discharge resistance. Silicone elastomeric adhesives and sealants retain their useful electrical properties at elevated temperatures because of their lack of degradation compared to many organic materials under similar oxidative conditions.

Typical RTV silicone elastomer electrical properties are shown in Table 3.

### APPLICATIONS

Because of their unique durability and elastomeric adhesive capabilities, silicone adhesive sealants have secured increasing market share in a wide variety of applications in the industrial,<sup>25</sup> construction,<sup>26</sup> and consumer markets. Over the past 25 years, they have lost categorization status as exotic specialty materials whose cost was justified only by lack of high-performing alternatives. A combination of higher organic materials costs and lower silicone manufacturing costs has, over the most recent decade, made silicone adhesives and sealants very cost-competitive for a large number of application areas, particularly when considered in the light of the superior properties that enhance their total cost-effectiveness. Industrial applications in particular seem to expand limitlessly as new demands for high-performance adhesive products continue to appear.

**Table 3. Typical RTV Silicone Elastomer Electrical Properties.**

Volume resistivity, ohm-cm	$3 \times 10^{15}$
Dielectric strength, volts/mil at 75 mil thickness	500
Dielectric constant @60 Hz	2.8
Dissipation factor @60 Hz	0.0026

### Industrial Adhesives and Sealants

One-component RTV sealants can be used to form both adherent and nonadherent gaskets that will withstand the extremes of the automotive engine environment. The *automotive* industry has for many years employed RTV silicones for oil-pan, valve-cover, water-pump, and many other sealing applications directly on engines where silicones' property advantages are needed. The valued properties are high-temperature durability, dimensional stability with age, minimal shrinkage during cure, adhesion to metal surfaces where required, and oil resistance. Of very great importance is the ease of application of these pastelike RTVs that will conform to surface irregularities and fill gaps that rigid, preformed, organic composition gaskets cannot; the need for finely machined surfaces is thereby reduced. The material is applied with automated robotic dispensing equipment, pumped from pails or drums. See Fig. 3. Aside from engines, gasketing with RTV silicone sealants is done on lens assemblies, transmission housings, rear axle covers and other mechanical assemblies where loss of grease or fluid or the prevention of intrusion of the elements is required.

Many other minor automotive applications exist for RTV adhesives, such as fastening mirrors and exterior trim in place; again the shock-absorbing nature of the RTV elastomeric adhesives as well as their long-term stability and weatherability are very desirable attributes in an environment of frequent temperature variations and constant vibration. A significant aftermarket exists for caulkers and collapsible tubes of the same products for use as repair material for gaskets when units are disassembled for repair, then regasketed for reassembly. Another automotive aftermarket application is for windshield gasketing when broken glass is replaced. See Fig. 4.

Two-component RTVs also have major automotive applications that take advantage of their superior electrical properties. All modern automobiles make use of electronic modules where protection is essential against shock, heat, water and dirt. Clear silicone potting gels serve these needs very well, and are widely used for this purpose; they conform to the elec-

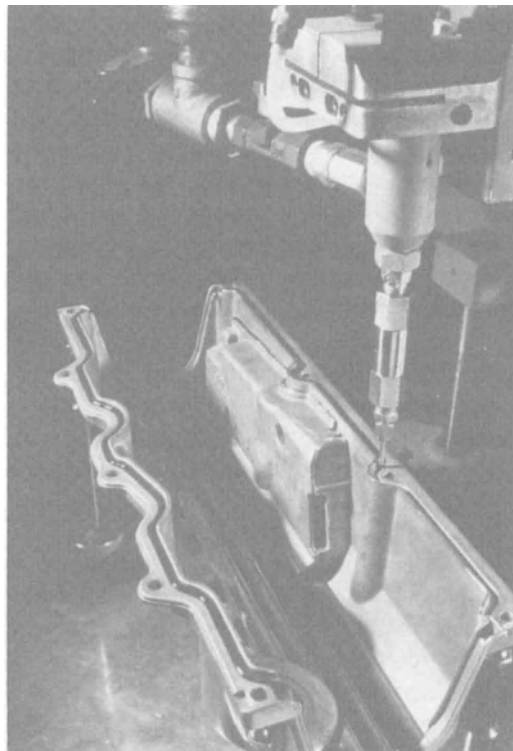


Fig. 3. Automated application of industrial sealant as automotive gasket.

tronic assemblies perfectly without shrinkage when applied either as conformal coatings or as encapsulants. The usual cure system for these products is a platinum-catalyzed addition reaction between vinyl and hydrogen groups on the siloxane molecules without the formation of any by-products; the reaction is initiated by heating rather than by exposure to atmospheric moisture characteristic of the one-component sealant cure systems described above. Another



Fig. 4. Aftermarket waterproofing of replacement windshield.

unique two-component silicone product used by some auto manufacturers is a gel that is cured within the mechanical parts of a bumper system to provide a shock-absorber for low-speed collision protection.

Beside the many automotive uses, one-component RTV products are applied in almost every segment of industry in which they can perform the functions of adhesives or as sealants and gaskets. As with the automotive applications, some end users dispense and apply RTVs from 55-gallon drums and from pails using pneumatic pumps; plastic cartridges of the product can also be employed either with power equipment or manually, and there are squeeze tubes for the smallest assembly and sealing work.

Many household *appliances*, from washing machines and steam irons to home electronic products employ silicone adhesive sealants as gaskets, to encapsulate electrical connections, and as general-purpose adhesives wherever good adhesion, electrical properties, temperature resistance, and longevity are required. Virtually all home aquarium manufacturers employ silicone sealants because of the excellent long-term bonding to glass and good clarity of the translucent products.

In *other manufacturing* applications, flowable one-component RTV silicones are used to coat circuit boards and encapsulate packaged electronic assemblies to isolate them from dirt, heat, water, and vibrational damage. These types of materials can be cut out and repaired if needed, as can be done with the gels described above.

*Aerospace* applications have always been extensive and are still growing, due to the outstanding resistance of these sealants to extremes of temperature and various forms of radiation. Sealants designed to emit virtually no volatile components in the high-vacuum environment of deep space are used to fasten solar panels in place and to perform other sealing functions in delicate satellite assemblies where stray condensable contaminants must be avoided near sensitive optical and electronic devices. Other sealants are used to fasten space shuttle tiles in place and for other applications where the maintenance of elastomeric properties is essential over a wide range of temperatures.

*Specialized products* are also made available by the major manufacturers to meet both general-purpose and very specific requirements. For example, as mentioned earlier, the continuous service temperature of an RTV sealant can be elevated to 550–600°F by compounding with *iron oxide*. RTV cure systems may exude either mildly acidic (acetic acid), neutral (methanol), or alkaline (cyclohexylamine) by-products, some of which may be contraindicated in certain applications such as on electronic assemblies. There is a general trend toward *neutral curing* sealants whose byproducts of cure are noncorrosive and less irritating to workers than acetic acid and amines. At least one sealant type is compounded to have low flammability, for applications (typically on aircraft) where this property is particularly important. *Fuel-resistant* adhesive sealants are made by using the *fluorosilicone* polymers mentioned earlier; the higher polarity of these materials confers resistance to swelling by hydrocarbon fuels, a property that is particularly prized in many aircraft applications.

### Construction Sealants

The outstanding resistance of silicone polymers to the effects of weathering that were mentioned earlier makes silicone sealants admirably suited to construction applications for *glazing* and a wide variety of *other waterproofing* functions. Generally medium- and low-modulus products have the greatest usefulness since they are better able to withstand movement (both expansion and contraction) of the parts of the structure that are being bridged by the sealant. Silicone sealants maintain their elastomeric properties for decades without cracking, splitting, shrinkage, chalking, or other degradation, in all types of climates. These sealants are also much more easily gunned and tooled at low temperatures than their organic counterparts, and they display excellent adhesion to a wide spectrum of ceramic, metal, and plastic substrates commonly employed in the construction industry, and usually without priming.

Because of their great elastic extensibility, the lower-modulus sealants are able to maintain waterproofing integrity in expansion joints hav-

ing relatively large movement requirements, at both high and low extremes of temperature.

The use of two-component silicone sealants as perimeter seals for insulated glass window units was mentioned earlier; recent trends in the construction of *curtainwall* buildings are towards the use of both two-part and one-part silicone adhesive sealants to bond these prefabricated glass panels to the metal elements of a building's structure, so that they function as structural adhesives in addition to acting as weatherproofing sealants to prevent the intrusion of air and water.

A very successful application of the weathering resistance of silicones has been made in *roofing*, where sprayable silicone rubber coatings have been applied for nearly twenty years over a number of substrates, most notably polyurethane foam. The foam is itself sprayed into place to serve as thermal insulation, and is then spray-coated with a fast-curing, two-component, self-bonding RTV elastomer to protect the system from weathering. Large structures can be covered with a monolithic seamless roof in this way, providing the benefits of energy conservation and long-lasting weatherproofing in one system.

### Consumer Sealants

The past decade has seen substantial growth in the consumer market for silicone sealants, driven by the lower cost of do-it-yourself repairs on houses, cars, and appliances.

New products have been developed beyond the familiar acetoxyl *bathub caulk* and translucent general-purpose *hobby glue*; these tend to be low-odor, neutral curing products designed to adhere without primer to an ever wider variety of substrates. They are made in a number of colors and are generally available in aluminum squeeze tubes and plastic caulkers; good packaging and shelf stability are important for sealants in this market because of lengthy distribution paths.

The familiar bathtub sealant containing a *mildewicide* is now on the market in a low-odor version. A number of *specialty automotive* products are available also, including high-temperature service products for engine gas-

keting such as on water pumps, thermostats, valve covers, etc.

Household sealant products in caulkers are used for myriad sealing, caulking and reglazing purposes inside and outside the home, most often for waterproofing any kind of exterior seam or joint. Here again the longevity of the sealant and avoidance of repeat caulking is a major silicone sealant advantage for the consumer.

### ABHESIVE ELASTOMERIC SILICONES

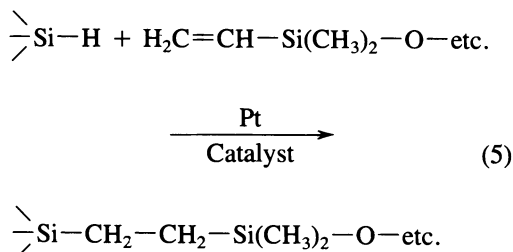
Crosslinked silicone polymer systems provide the basis for a large class of products that are adhesive, or release agents, in contrast to the adhesive products discussed above. Many useful applications exist for these materials, the most widely known one being *silicone release coatings* for labels, and for packaging and other applications where one surface must be able to release from another adhesive-coated surface when required. *RTV molding products* constitute another major class of release-type products.

A low-energy surface film is required for abhesion, and dimethylpolysiloxane films have the lowest surface energy of any polymers except the perfluoroethylenes. For that reason, silicone surfaces are extremely capable of releasing pressure sensitive adhesives or other tacky materials. The adhesives discussed earlier are usually compounded with adhesion-promoting polar additives and tend to develop adhesive links to substrates during the cross-linking process; their cured exposed surfaces nevertheless also show low surface energy, and are not easily adhered to by organic adhesives. A film of a cured silicone release agent may be envisioned as if the polar oxygen atoms of the siloxane chains were oriented internally toward the substrate, with a layer of low-polarity methyl groups bonded to silicon atoms presenting at the releasing surface of the film. This structure evidently prevails regardless of how the silicone film is applied or cured.

### Molding Compounds

RTV molding compounds take advantage of this release capability by enabling the exact du-

plication of minute detail in parts cast in silicone rubber molds. Typically the RTV is of the addition-cure type in which the siloxane chains are extended and crosslinked by the chemical addition reaction of an Si—H containing crosslinking polymer and a dimethylpolysiloxane polymer terminated with vinyl groups:



There are no chemical byproducts of this reaction, and the soluble platinum catalyst can be effective at as little as 5ppm concentration. Although it is basically a room temperature curable two-part system, heat is customarily used to accelerate the process for economic and productivity reasons. The RTV is mixed, poured over a master, and heat-cured. Organic polymer parts (polyurethanes, polystyrene, etc.) can then be poured in the silicone rubber mold and later easily released, with highly effective reproduction of fine details. This type of molding product has found many uses in the furniture industry for the production of intricate decorative simulated-wood parts, and in general for molding a myriad of decorative items. An even more flexible type of elastomeric molding compound has been marketed that is based on silanol condensation cure chemistry rather than the vinyl-hydride addition cure just described. These lower modulus products are designed to be softer, with good tear resistance; these properties allow even more intricate and undercut

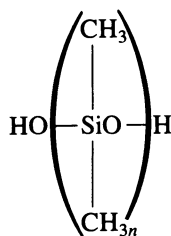
parts to be cast and successfully demolded, still with excellent reproduction of fine detail.

### Release Coatings

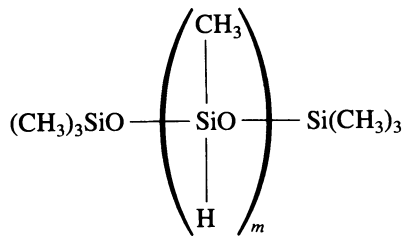
Release products are fundamentally reactive RTV products sold as two or more components that are mixed to form a coating bath. The blended mixture is then coated onto a substrate by one of a number of techniques that will enable the deposition of a uniform film of the desired thickness. The coated stock is then passed through an oven with a suitable combination of residence time and temperature that will cure the silicone by completing the crosslinking reaction with thermal energy.

This class of materials, regardless of the type of cure chemistry employed, is referred to as thermally cured, although in fact the curing reaction does begin at room temperature as soon as the components of the product package (reactive silicone polymers, crosslinkers, catalysts, inhibitors, and sometimes dispersants) are mixed to form the coating bath. Such factors as polymer molecular weight, the use of a dispersing medium, and the coating methods required for a particular product package, are all derived from the need to maintain the product as a coatable liquid in the coating pan while still enabling rapid crosslinking to occur after application of the coating on the substrate.

Thermally cured release coatings generally employ either the vinyl-hydride addition cure chemistry described above for the molding compounds<sup>27</sup> or another fast-acting chemical system based on the condensation reaction between a silyl hydride crosslinking polymer (of low molecular weight) and a silanol-terminated polymer of the same type as described in the earlier section on adhesive sealants, but of a much higher molecular weight:

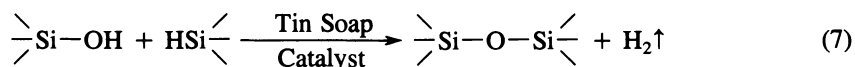


Silanol Polymer  
(*n* greater than 4000)  
for solvent-based products



Methyl Hydrogen  
Silicone Polymer  
(*m* = 10 to 50) (6)

The reaction for crosslinking is:



Silyl hydride (SiH) groups are very reactive and the above-described condensation reaction occurs with such ease that a catalyzed mixture of the two principal reactants will gell at room temperature. Solvent dispersion of the mixture is commonly used to overcome this reactivity by dilution, and also to provide a means of coating what would otherwise be a very high viscosity polymer mixture onto the substrate.

Release systems based on this condensation cure chemistry are commonly sold as two-part packages. One (A) is a high-solids solution of the silanol-terminated high viscosity polymer (commonly called a *gum*) plus the methylhydrogen crosslinker. The second part (B) is a solution of the tin soap catalyst. Further dilution of the A and B mixture is then done with more solvent to achieve an approximate 5–10% solids content; the bath is then adequately coat-able by techniques such as reverse roll, rotogravure, metering rod, or doctor blade.

To raise the solids content or to render the system totally solventless, the molecular weight (and viscosity) of the silanol polymer must be drastically reduced, but the working life of such a solventless system becomes only a few minutes at room temperature. This becomes impractical, and since there is no known means of inhibiting the tin soap catalyst (necessary for completion of the thermal crosslinking reaction), other chemical systems are needed for truly solventless coatings.

Solventless release coating systems are where the vinyl-hydride addition chemistry shown in Eq. (5) becomes of great value because of its versatility. First, the polymer's molecular weight (hence viscosity) can be reduced to the low values required for coating without solvent dilution. The noble metal catalyst (platinum- or rhodium-derived) is dissolved in it, along with a chemical which inhibits its activity at room temperature. Thus when a coating batch is made by mixing in the methylhydrogen crosslinker before use, the blend is stable at room temperature so as to provide an acceptable pot life not possible without the inhibitor. When

heated after coating, the inhibitor decouples from the catalyst and the crosslinking reaction proceeds rapidly.

A very important feature of the solventless systems is that no thermal energy input is required for the evaporation of a solvent; all the heat goes into the curing reaction. A second major advantage is that no solvent-recovery equipment is needed, which avoids both a considerable capital expense and a significant environmental regulatory concern.

The force required to separate an adhesive from a silicone release coating can be modified over a wide range by varying the polymer system's molecular weight characteristics. Elastomeric coatings formed from densely crosslinked low molecular weight polymers tend to have harder, more resinlike characteristics that allow easier release of adhesives. Coatings derived from high molecular weight gums with more widely spaced crosslinks tend to be more rubbery in character and to be less adherent, consequently requiring more force for separation (higher release types). A fairly recent innovation in solventless systems has been the separation of these systems into their components, for sale as packages of tight release polymer, easy release polymer with catalyst, inhibitor, crosslinker and easy release polymer alone; the converter is thus provided with a greater degree of flexibility to formulate a coating bath to meet his particular needs by tailoring cure rate, bath life, and release characteristics for his particular application.

Since release coatings are now ubiquitous in many familiar packaging and labelling applications, the number of substrates to which they are applied has also multiplied. One of the most common ones is supercalendered kraft paper, upon which coatings are usually deposited at the rate of about a gram per square meter to give good coverage. There are now many non-porous films to which silicone release coatings are applied, including a variety of plastic films: polyethylene and polyethylene terephthalate are typical.

The selection of a coating system can be complicated by a number of considerations. The temperature and time of cure has to be considered versus the heat stability of the substrate plastic or paper. The degree of dimensional change and/or moisture loss of the substrate during cure at a particular time and temperature profile is a factor, also. Another consideration is the tendency of the uncured coating to penetrate the substrate before and during cure, which is also related to the attainability of a pinhole-free coating for efficient release.

### Radiation-Curable Coatings<sup>28,29</sup>

Major silicone suppliers have been developing radiation-curable coatings for some time now; the solventless systems lend themselves to this approach since all the space radiant energy can be directed at the polymer system for curing, and none wasted for solvent evaporation or in the substrate. The energy source referred to may be either ultraviolet or electron-beam radiation, and the objective is a very rapid "zero-temperature" controllable cure, with much of the control occurring through the intensity of the source.

However attractive in principle, there are certain inherent drawbacks in this chemistry that might prevent radiation-curable silicones from making more than modest inroads into the markets for thermal-cure products. There is a necessity for a high concentration of radiation-sensitive organic functionality in the radiation-curable polymer systems, for standard silicone polymers are not sensitive to UV or EB radiation in economically useful doses. Silicone polymers modified with the necessary acrylate, epoxy, or mercaptan functional groups are more expensive; furthermore organic photosensitizers are needed in significant quantities, and these are generally poorly soluble in silicones. Polar organic constituents tend also to raise release values and to render the cured coatings more susceptible to instability in contact with certain aggressive adhesives.

Nevertheless, chemical and engineering work is continuing in this area in an attempt to take advantage of the opportunities in the market-

place for release coatings that are curable with low energy expenditure, have lower space requirements for processing, allow higher line speeds, and application to thermally sensitive substrates.

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# Organofunctional Silane Coupling Agents

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The development and increasing use of organofunctional silanes has closely paralleled the growing use of composite materials in expanding and diverse applications. From the crude laminates developed to meet the material shortages of World War II, composite materials have evolved into sophisticated products that are required to meet ever increasing performance demands. In addition to providing a wide range of mechanical properties, many of today's composites are asked to furnish specific electrical characteristics, lend themselves to various fabrication techniques, maintain their properties after exposure to hostile environments, and accomplish this in an economically viable manner. The challenge is indeed great.

The composites of this discussion are combinations of organic polymers and glass fibers and/or particulate fillers. Included among the useful organic polymers are both thermosetting and thermoplastic resins and elastomers. Glass fibers are used in many forms including continuous roving, chopped strand, mat, and woven fabric, the choice indicated by fabrication method and/or property requirements. The particulate fillers encompass a wide range of materials including refined natural minerals and synthetic products. Prominent among these are clays, silicates, and silicas.

The high strength and modulus of glass fibers

have made them obvious candidates as reinforcements for organic polymers; however, the function of particulate fillers has evolved with time. Originally, except for the use of selected fillers as reinforcements for elastomers, fillers were used to control rheology and to lower the cost of the composite. More recent developments have shown that fillers can, particularly with surface modification, make positive contributions to composite properties while continuing to affect rheology and costs.

Common to all of the composites discussed is a large interfacial area between the organic polymer and the fiber and/or filler. To optimize both the ease of fabrication and the resulting composite properties, it is necessary that as a minimum the organic polymer wet the fiber or filler surface and ideally that it bond to it. This chapter is concerned with the use of organofunctional silicon compounds to promote the wetting of the fiber/filler surface, establish bonds between the polymer and the fiber/filler, and retain these bonds under a hostile environment.

## THEORY

The matrix resin of a modern mineral reinforced organic resin composite serves many functions. It influences the method used to fab-

ricate the composite, it limits the environment in which the composite may be used (solvent resistance, ozone resistance, etc.), it limits useful temperature range (oxidation, depolymerization), and it influences the economics of the composite. However, its most critical function is to transfer stress applied to the composite to the high modulus mineral phase. In order to efficiently transfer stress from the low modulus matrix resin to the high modulus mineral reinforcement, it is necessary that the matrix resin adhere to the mineral reinforcement. In addition, if the composite is to have practical utility, the adhesion must be retained under typical use conditions, commonly high humidity and elevated temperatures.

The absence of direct measurements at the interface has led to considerable speculation as to the preferred mechanism for improved interfacial adhesion.

Bikerman<sup>1</sup> contended that an adhesive failure should be considered highly unlikely; that the intermolecular forces at an interface are stronger than the cohesive strength of either component.

Zisman<sup>2</sup> emphasized the requirement that the resin must wet the reinforcement to achieve the desired adhesion. He described the requirements of wetting as the surface tension of the matrix resin being less than the surface energy of the reinforcement. These conditions would appear to be met by the use of most thermosetting matrix resins and untreated reinforcement (heat cleaned fiberglass), yet these combinations produce composites with lower mechanical properties, both dry and wet, than produced with silane treated reinforcement. A probable explanation is that the presence of water on the surface of the untreated reinforcement interferes with or prevents complete wetting of the reinforcement by the matrix resin.

A different method for bonding dissimilar materials such as organic polymer and fibrous glass has developed in the field of reinforced and filled plastics. This approach utilizes a coupling agent, i.e., a bifunctional material, that is capable of reacting with and forming covalent chemical bonds with both the organic polymer and the substrate. Silane coupling agents are organofunctional silane monomers (Table 1) that possess a dual reactivity. This

characteristic enables groups at one end of the molecule (usually chloro, alkoxy, or acetoxy) to hydrolyze, and form silanols (SiOH), which are then able to condense with similar groups on glass or other siliceous substrates. In the case of metals, or other nonsiliceous substrates, condensation of SiOH with metal oxides or hydrolysis of ester groups with monolayers of water on the surface is possible. At the other end of the silane molecule are organic groups, such as vinyl, methacryloxy, amino, epoxy, or mercapto, which are able to coreact with the organic matrix resin.

The bridging of the interface between resin and reinforcement by a coupling agent provides good adhesion, and the stability of the covalent linkage maintains this adhesion under high humidity. It is recognized that good wetting is desirable, both to speed the fabrication of composites and to promote contact between the various components, thus making the necessary chemical reactions more efficient.

One of the first comprehensive studies on the mechanism of silane reaction at the interface was reported by Sterman and Bradley.<sup>3</sup> Their work established three significant points: (1) greater than theoretical monolayers of silane on fiberglass were required to achieve optimum composite performance because of the accumulation of silane in the capillaries between glass fibers, (2) silane coupling agents are tenaciously bonded to fiberglass when applied from aqueous solution and dried, and (3) the chemistry of the organofunctional group on the silane must be matched with that of the matrix resin to develop optimum composite properties.

Plueddemann and co-workers<sup>4</sup> confirmed this latter point when they published the performance of a wide range of organofunctional silanes in both unsaturated polyester and epoxy composites.

Marsden<sup>5</sup> described the composition and performance of a series of organofunctional silanes that provide amine reactivity but vary in compatibility with the matrix resin, provide lubricity, and ionic types that provide antistatic effects. These silanes are of two types:  $\text{ROOCCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{SiX}_3$  and  $[\text{R}_3\text{NCH}_2\text{CH}_2\text{CH}_2\text{SiX}_3]^+\text{Cl}^-$ . In each case the R group was varied to change compatibility

Table 1. Recommended Organofunctional Silane Coupling Agents for Various Resins.

Union Carbide Silane	Chemical Name	Thermosetting <sup>a</sup>	Thermoplastic <sup>b</sup>	Elastomers <sup>c</sup>	Dow Corning Silane
A-143	$\gamma$ -Chloropropyltrimethoxysilane	Epoxy	Nylon		Z-6076
A-150	Vinyltrichlorosilane	Polyester			
A-151	Vinyltriethoxysilane	Polyester			
A-172	Vinyl-tris( $\beta$ -methoxyethoxy) silane	Polyester			
A-174	$\gamma$ -Methacryloxypropyltrimethoxysilane	Polyester, vinyl ester	Polystyrene, polyethylene ABS, polypropylene	EPM, EPDM, BR XLPE	Z-6030
A-186	$\beta$ -(3,4-Epoxychlorohexyl) ethyltrimethoxy-silane	Polyester, epoxy	Polystyrene, polyethylene ABS, SAN, nylon, TP polyester		
A-187	$\gamma$ -Glycidoxypentyltrimethoxysilane	Polyester, epoxy			Z-6040
A-188	Vinyltriacetoxysilane	Melamine, phenolic	Acetal		
A-189	$\gamma$ -Mercaptopropyltrimethoxysilane	Polyester			
A-1100	$\gamma$ -Aminopropyltriethoxysilane	Epoxy, phenolic			Z-6062
A-1120	N-( $\beta$ (aminoethyl)- $\gamma$ -aminopropyltrimethoxy)silane	Epoxy, melamine Phenolic	Nylon, polycarbonate PVC, PP, PE, PMMA, TP polyester, PPO	NR, IR, BR, SBR, EPM, EPDM, CR, NBR	Z-6020
A-1160	$\gamma$ -Ureidopropyltriethoxysilane	Epoxy, melamine Phenolic	Nylon, PVC		
A-1111	bis( $\beta$ -hydroxyethyl)- $\gamma$ -aminopropyltriethoxysilane	Epoxy	Acetal, polycarbonate polysulfone, nylon		
A-1106	Aqueous solution of $\gamma$ -aminopropyl silane	Epoxy, melamine	Nylon		
A-1128	Proprietary amino Vinylbenzylamine functional silane	Epoxy Epoxy, polyester	Nylon, polyolefins		Z-6032

<sup>a</sup>Thermosetting resins make use of the Silanes listed on the same line. In addition, A-1100 and A-1120 are suitable for either epoxy, melamine or phenolic.

<sup>b</sup>The thermoplastic resins polystyrene, polyethylene, ABS and polypropylene use either A-174 or A-186 while polystyrene, ABS, SAN, nylon and TP Polyester are served by A-186 or A-187. Nylon . . PPO make use of either A-1100 or A-1120.

<sup>c</sup>The four elastomers headed by EPM . . are coupled with the aid of A-151, A-172 or A-174. The eight elastomers headed by NR . . require A-189, A-1100 or A-1120.

with the matrix resin and lubricity of treated fiberglass and in the case of the ionic silanes to provide anti-static effects. While these materials have not as yet found commercial acceptance in fiberglass sizes, they do offer another way to affect some of the important properties of fiberglass reinforcement.

During this period there were several attempts to interpret the effect of chemical coupling between resin and reinforcement on the mechanics of the interface. Kumins and Roteman<sup>6</sup> proposed a boundary layer, including the silane coupling agent, of intermediate modulus between the resin and the reinforcement. Erickson<sup>7</sup> suggested that the reinforcement and/or silane coupling agent could selectively adsorb components of the resin and modify the properties of the resin at the interface relative to the bulk resin.

A stress-relaxation mechanism was proposed by Plueddemann<sup>8</sup> that postulated the formation and hydrolysis of stressed bonds between coupling agent and reinforcement in the presence of water. He also requires that the resin at the interface be rigid, not rubbery. The requirement of a rigid interface may be true for reinforced resins; however, the excellent reinforcement obtained by the use of silane coupling agents in mineral filled rubber raises some interesting questions. Do the reinforced resin and the reinforced rubber function by the same mechanism? Does the interaction of silane/rubber/filler result in a rigid interface in an overall elastic system? These questions remain to be resolved.

In summary, organofunctional silanes have been extremely effective in improving and maintaining the properties of reinforced composites by providing adhesion between the matrix resin and the reinforcement. A variety of silane coupling agents are commercially available that appear to meet current requirements, particularly for the thermosetting resins. The newer technologies, the use of silane coupling agents in reinforced thermoplastics and elastomers, are just developing. Their requirements in terms of interface modification are in the process of being defined. Products are being made and used with today's silane coupling agent technology; optimizing the potential

properties of these systems offers a challenge to workers in several disciplines.

## APPLICATIONS

Perhaps the most meaningful confirmation of the efficacy of organofunctional silanes in improving and maintaining the properties of reinforced composites is the use of these materials in commercial applications. A listing of end uses of composite materials is almost endless and is growing daily. The purpose of this section is to discuss some of the uses in general and to indicate the magnitude of property improvements that can be obtained by the use of silane coupling agents.

### Thermosetting Resins

Fiberglass-reinforced thermosetting resins were for many years the entire composites industry. The development of organofunctional silanes as interface modifiers was carried out using thermosetting resins, and this application area justified the original commercialization of silane coupling agents. The range of properties that can be produced by composite materials is aptly demonstrated in the reinforced thermosets. High performance is achieved by the use of fiberglass filament wound composites, while the low end of the performance scale is served by particulate filled resins. In the area of fiberglass reinforced composites, required strength can be designed into the composite by the choice of the amount and orientation of the fiberglass used. Table 2 indicates the range of flexural strengths that can be obtained using a general purpose polyester resin and various forms of readily available fiberglass reinforcement.

**Table 2. Flexural Strength of Various Glass Reinforced Polyester Resin Composites.<sup>a</sup>**

	Glass Content (wt%)	Flexural Strength (psi $\times 10^{-3}$ )
Chopped strand mat	35-45	30-40
Woven roving	55	40-50
Satin weave cloth	62	65-90
Unidirectional roving	70	150-180

<sup>a</sup>General-purpose polyester resin; commercial reinforcements.

The choice of a particular thermosetting resin for a specific composite application is governed by a number of factors. Among these are cost, cure conditions, use temperature, electrical properties, etc. All of the thermosetting resins can be reinforced with fiberglass; for optimum performance, each will require a silane coupling agent on the glass selected to match the chemistry of the resin. Table 3 shows the effect a properly selected silane can have on the initial and retained properties of composites produced from four different thermosetting resins.

In addition to the use of fiberglass to reinforce thermosetting resins, large amounts of particulate fillers are used with thermosetting resins to produce composites. The reasons for adding a filler to a resin are many: to reduce costs, control rheology, reduce shrinkage, etc. In many cases, however, the addition of a filler produces a significant loss in both mechanical and electrical properties, particularly after exposure to water. The use of an organofunctional silane, either integrally blended into the resin-filler mix or pretreated onto the filler surface, can prevent or greatly minimize the losses. Typical of the results that can be achieved are shown in Table 4. This table describes the effects produced by several silane coupling agents on the mechanical and electrical properties of an epoxy resin filled with three different mineral fillers. The retention of electrical properties after water exposure is particularly impressive.

**Table 3. Effect of Silanes on Glass Reinforced<sup>b</sup> Thermoset Resins.**

Resin System	Silane	Flexural Strength	
		Dry	Wet
Polyester	control	60,000	35,000
	A-174	87,000	79,000
Epoxy	control	78,000	29,000
	A-186	101,000	66,000
Melamine	control	42,000	17,000
	A-187	91,000	86,000
Phenolic		dry	high temperature <sup>a</sup>
	control	69,000	14,000
	A-1100	85,000	50,000

<sup>a</sup>Aged 100 hr at 500°F and tested at 500°F.

<sup>b</sup>181 style woven glass cloth.

The same type of strength improvement is found in foundry cores or shell molds when silane coupling agents are used. Foundry shell molds are thin-walled, fragile composites of sand and resin which permit the casting of various precise units especially for the automotive industry. Aminosilane addition to a phenolic or furan/sand mixture results in stronger molds and cores that resist handling damage and degradation in adverse environments. Tables 5 and 6 illustrate the options that are available with silane addition. One can achieve increased performance at the same resin concentration or equivalent performance at reduced resin concentration.

Table 7 illustrates that a much stronger aluminum oxide filled grinding-wheel composite results with aminosilane coupling agent than without. A greater safety margin for wheels is achieved during frictional heat buildup and under wet grinding conditions.

The concept of a metal filled resin is useful in the tool and die industry, where in certain applications the costly, time-consuming fabrication of solid metal molds is being replaced by relatively inexpensive, easily fabricated metal filled resin systems. Table 8 shows how silane coupling agents can offer strength improvement in this composite system.<sup>9</sup>

Sand filled epoxy resins find utility as simulated terrazzo flooring, concrete highway and bridge abutment repair kits, and in various other applications where a concrete substitute is required that is convenient to use and cures rapidly. Table 9 indicates the strength improvements that can be produced in these systems by the use of silane coupling agents, both initially and after environmental aging.

### Thermoplastic Resins

The coreactivity of organofunctional silanes with highly reactive thermosetting resins during cure is not unexpected and offers a ready explanation for the specificity shown by a given resin for an optimum performing silane. However, thermoplastic resins are normally considered rather completely reacted and quite inert under normal process and molding conditions. It is, therefore, surprising that a similar specificity between resin and organofunctional si-

**Table 4. Effect on Flexural and Electrical Properties of Silane Additives to Filled Epoxy Resin Composites.<sup>a</sup>**

Filler/Silane <sup>b</sup>	Flexural Strength (psi × 10 <sup>-3</sup> )		Dielectric Constant <sup>c</sup>		Dissipation Factor <sup>c</sup>		Volume Resistivity (ohm/cm)		Dielectric Strength (V/mil)	
	Dry	Wet <sup>e</sup>	Dry	Wet <sup>e</sup>	Dry	Wet <sup>e</sup>	Dry	Wet <sup>e</sup>	Dry	Wet <sup>e</sup>
Clear resin	18.1	16.0	3.44	3.43	0.007	0.005	> 8.2 × 10 <sup>16</sup>	> 8.1 × 10 <sup>16</sup>	> 414	> 413
50% Wollastonite <sup>d</sup> Nyc										
Control (no silane)	15.8	9.8	3.48	22.10	0.009	0.238	4.9 × 10 <sup>16</sup>	3.3 × 10 <sup>12</sup>	> 391	77.6
A-186	18.1	13.3	3.42	3.57	0.014	0.023	1.9 × 10 <sup>16</sup>	2.4 × 10 <sup>15</sup>	> 400	388
A-187	18.7	15.2	3.30	3.42	0.014	0.016	1.8 × 10 <sup>16</sup>	1.2 × 10 <sup>15</sup>	> 356	372
A-1100	16.7	12.6	3.48	3.55	0.017	0.028	1.2 × 10 <sup>16</sup>	2.0 × 10 <sup>15</sup>	> 408	> 410
50% Minusil 10μ <sup>f</sup>										
Control (no silane)	22.4	10.3	3.39	14.60	0.017	0.305	> 8.4 × 10 <sup>16</sup>	5.1 × 10 <sup>11</sup>	> 381	103
A-186	22.0	14.5	3.48	3.52	0.016	0.023	> 8.0 × 10 <sup>16</sup>	1.4 × 10 <sup>15</sup>	> 367	> 360
A-187	23.2	21.4	3.40	3.44	0.016	0.024	> 8.2 × 10 <sup>16</sup>	1.7 × 10 <sup>15</sup>	> 357	> 391
A-1100	20.0	12.0	3.46	3.47	0.013	0.023	> 8.1 × 10 <sup>16</sup>	1.8 × 10 <sup>15</sup>	> 355	> 355
50% ASP-400 <sup>g</sup>										
Control (no silane)	14.1	10.0	4.35	8.07	0.018	0.163	3.5 × 10 <sup>16</sup>	4.2 × 10 <sup>13</sup>	> 344	280
A-186	12.4	10.7	3.43	6.54	0.012	0.059	2.4 × 10 <sup>16</sup>	2.5 × 10 <sup>15</sup>	> 375	> 407
A-187	14.6	11.1	3.17	3.26	0.012	0.093	1.8 × 10 <sup>16</sup>	1.4 × 10 <sup>14</sup>	> 382	> 356

<sup>a</sup>Composites contain 50 wt% filler in 100 parts ERL-2774 Resin (Union Carbide Plastics Division), 80 parts MNA & 0.5 parts BDMA.<sup>b</sup>Silane loading base on filler is equal to a monomolecular layer.<sup>c</sup>Tested after 72 hr immersion in boiling water.<sup>d</sup>Interpace Corporation.<sup>e</sup>Measured at 1000 cycles according to ASTM D-150.<sup>f</sup>Crystalline silica, Pennsylvania Glass Sand Corp.<sup>g</sup>Kaolin Clay Minerals and Chemicals Division, Phillip Corp.**Table 5. Effect of A-1100 on Shell Molds Using Phenolic Resin and Foundry Sand.<sup>a</sup>**

Phenolic Resin Solids Content	Control	A-1100 (0.025 wt% based on sand)	Percentage Improvement
3.5%	587	777	32
2.5	too resin-poor to mold		

<sup>a</sup>Tensile strength of molded "dog bone" specimens.**Table 6. Effect of Amino Silane Coupling Agent A-1100 in Furan Resin<sup>a</sup> Binder for Foundry Sand Composites.**

% Binder	% A-1100 (based on binder)	Tensile Strength, psi		Scratch Hardness		Work Life, min
		65% R.H.	93% R.H.	68% R.H.	93% R.H.	
2.0	0	153	84	94	93	14
2.0	0.4	318	248	95	93	15
1.2	0	120	68	89	80	25
1.2	0.4	212	115	93	85	28

<sup>a</sup>Data obtained by Quaker Oats, Ltd. Chemical Research Division on a "no bake" composite containing furan binder, lake sand, and catalyzed with 35% phosphoric acid (85%).

**Table 7. Effect of Amino Silane Coupling Agent A-1100 on Flexural Strength of Phenolic Resin Bonded  $\text{Al}_2\text{O}_3$  Composites.<sup>a</sup>**

$\text{Al}_2\text{O}_3$ Grit Size	Dry Flexural Strength, psi		% Flexural Strength Improvement
	No Silane	With Silane	
12	2070	3060	+48
20	2988	4086	+37
36	4176	5328	+28
60	5544	6408	+16

<sup>a</sup>These test composites were formulated to contain 92 wt%  $\text{Al}_2\text{O}_3$  and 8 wt% of an 80/20 mixture of powdered and liquid phenolic resin. A-1100 is applied at 0.1 wt% based on grit weight.

**Table 8. Effect on Flexural and Compressive Strength of Silane Addition to an Epoxy-Aluminum Composite.<sup>a</sup>**

Silane Additive	Flexural Strength, psi		Compressive Strength, psi	
	Initial	72 hr $\text{H}_2\text{O}$ Boil	Initial	72 hr $\text{H}_2\text{O}$ Boil
None	620	470	2,110	2,100
1 wt% A-1100	1,240	1,310	2,970	3,220
1 wt% A-186	1,240	1,200	3,700	3,990
1 wt% A-187	1,110	1,030	3,230	3,430

Flexural and compressive strength specimens were cut from these castings after a cure of 16 hr at room temperature followed by 2 hr at 350°F.

<sup>a</sup>61.5 wt% aluminum needles.

lane treated reinforcements exists in thermoplastic composites.

Both Plueddemann<sup>10</sup> and Sterman and Marsden<sup>11</sup> published on the use of organofunctional silanes in glass reinforced thermoplastic. Plueddemann divided thermoplastic resins into "reactive" and "nonreactive" categories. He

proposed that the reactive polymers chemically react with the silane coupling agent, while the nonreactive polymers exhibit compatibility with the silane treated surface as indicated by solubility parameters. Sterman and Marsden, while recognizing that wetting of the silane treated surface by the matrix resin is desirable, pro-

**Table 9. The Effect of Addition of Various Silanes to Sand Filled Epoxy Resin Composites.**

Resin Content, %	Specimen Conditioning	Tensile Strength, psi			
		Control (no silane)	A-187 <sup>a</sup>	A-1100 <sup>a</sup>	A-186 <sup>a</sup>
15.0	dry	925	1,225	1,030	1,040
	freeze-thaw <sup>b</sup>	500	800	835	790
	8 hr $\text{H}_2\text{O}$ boil	215	440	355	500
12.5	dry	850	1,150	1,120	900
	freeze-thaw <sup>b</sup>	—	435	740	510
	8 hr $\text{H}_2\text{O}$ boil	110	260	285	300
10.0	dry	705	730	750	570
	freeze-thaw <sup>b</sup>	—	155	190	120
	8 hr $\text{H}_2\text{O}$ boil	110	140	200	145

<sup>a</sup>Silane concentration was 0.1 wt% based on sand.

<sup>b</sup>Freeze-thaw cycle: 24 hr immersion in R.T. Water; 8 hr at  $-30^\circ\text{C}$ ; 16 hr at R.T.

pose chemical bonding between matrix resin and silane as the most likely mechanism for the reinforcement of thermoplastic resins by silane treated fiberglass. In a subsequent publication<sup>12</sup> they showed that the reaction between an olefinic silane and a nonreactive resin such as polypropylene could be promoted by the addition of a free radical source. Table 10 indicates the magnitude of strength improvement that can be produced by the use of a silane coupling agent in a glass fabric reinforced composite utilizing a variety of thermoplastic resins.

If the promise of glass reinforced thermoplastics is to be realized, the composites must be fabricated by high speed, low unit cost injection molding of chopped glass reinforced resins rather than the slower techniques for producing the prototype laminates shown in Table 10. The injection molding method places stringent requirements on the glass fiber size. In addition to coupling the matrix resin to the glass, the silane must protect the glass during the high shear mixing and allow good dispersion of the fibers in the matrix resin.

The fiberglass producers have done an outstanding job in this regard. Tables 11–13b show some of the properties of injection molded composites of 30% glass/70% resin using nylon, poly(butylene terephthalate) and polypropylene, respectively. In all cases, the use of unsized virgin roving produces strengths greater than that of the neat resin; and as predicted by Table 10 the use of a silane coupling agent produces a significant gain over virgin glass. However, in each case, the highest values are

achieved with a complete size that lubricates and protects the glass as well as allowing the contained silane coupling agent to develop adhesion between the glass and matrix resin.

The use of conventional organofunctional silanes, as described in the section on filled thermosetting resins, has been tried in filled thermoplastic resins with mixed results. Orenski and co-workers<sup>13</sup> reported good results with the use of Union Carbide A-187 and A-1100 in wollastonite filled engineering resins at high filler loading. Attempts to extend this approach to less reactive thermoplastic resins, such as polyolefins, were less successful.

A different approach has been proposed to enhance the properties of filled thermoplastics, utilizing a family of *organosilicon chemicals*. This new approach proposes that coupling the matrix resin to the inorganic filler is necessary but not sufficient to optimize the overall properties of the composite. The organosilicon chemicals provide multifunctional reinforcement promotion effects at the filler-matrix boundary, including (1) coupling the filler to the matrix resin and (2) modifying the matrix resin in the region near the filler particle. These inter-phase modifications result in improved composite mechanical properties, increased impact strength, improved filler dispersion, and higher extrusion throughput rates. In selected resins, these matrix modifications also result in higher heat distortion temperatures and the coupling chemistry employed provides improved long term heat aging.

The first products resulting from this ap-

**Table 10. Effect of Silane Finishes on Mechanical Properties of Glass Cloth Reinforced Thermoplastic Resins.<sup>a</sup>**

Resin	Silane	Flexural Strength % Improvement Over Control <sup>b</sup>		
		Dry	Wet <sup>c</sup>	Elevated Temp. (°F)
Polystyrene	A-174	100	95	70 (200)
Polyvinyl chloride	A-1111	83	100	—
Nylon	A-1111	110	160	150 (400)
Polycarbonate	A-1100	30	60	20 (250)
Polymethyl methacrylate	A-1100	45	90	25 (200)
Acrylonitrile-butadiene-styrene	A-187	145	228	145 (150)

<sup>a</sup>Laminates contain 11 plies of 181-type glass cloth, 40–45% resin.

<sup>b</sup>Control is heat-cleaned glass cloth reinforcement.

<sup>c</sup>Immersion for 16 hr in water at 120°F.



**Table 11. Physical Properties of Glass Reinforced Nylon 6,6 (0% Glass–70% Nylon 6.6).**

Size	Flexural Strength psi	Flexural Modulus psi × 10 <sup>5</sup>	Tensile Strength, psi		Tensile Modulus, psi × 10 <sup>5</sup>		Heat Distortion Temp. °F (°C)
			Dry	Wet	Dry	Wet	
Commercial No. 1	39,100	11.1	25,800	21,600	17.4	14.4	487(253)
Commercial No. 2	30,800	9.3	21,400	18,800	16.8	13.2	492(255)
A-1100	24,900	7.7	14,800	14,600	15.8	11.4	498(259)
A-1160	29,200	7.4	18,700	16,400	14.4	12.2	472(244)
A-186	30,100	9.3	22,400	19,000	16.0	13.2	473(245)
A-187	31,300	10.0	20,500	15,800	15.2	14.4	481(249)
Virgin roving	17,100	8.1	10,000	8,600	15.4	10.4	459(237)
No glass	12,600	2.4	8,900	8,300	3.1	2.7	165(74)

proach were introduced by Godlewski<sup>14</sup> for polyolefin/mica composites. The use of this two-component additive package, Union Carbide PC-1A and PC-1B (proprietary compositions), produce significant property enhancement in mica filled polypropylene and mica filled high density polyethylene, as shown in Tables 14 and 15. These materials may be used to pretreat the mica or they may be integrally blended during compounding. In addition to property enhancement, the use of these products are claimed to increase extrusion rate. While these products were originally introduced for use in filled polypropylene, recent

work<sup>15</sup> has shown they appear to be equally useful in glass fiber reinforced polyolefins. The results shown in Table 16 indicate that the use of PC-1A and PC-1B produces significant property improvements in a glass fiber reinforced polypropylene composite that contains a polypropylene compatible reinforcement.

The continuing interest in changing the combustion characteristics of composites has focused attention on ATH (alumina trihydrate) filled high density polyethylene. Attempts to incorporate high loadings of ATH into HDPE normally leads to processing difficulties and degradation of composite properties.

**Table 12a. Dry Physicals of Glass-Reinforced PBT.<sup>a</sup>**

Size	Flexural Strength, psi	Flexural Modulus, psi × 10 <sup>5</sup>	Tensile Strength, psi	Tensile Modulus, psi × 10 <sup>5</sup>	Izod Impact Strength		Heat-Distortion Temperature, <sup>d</sup> °F(°C)
					Notch <sup>b</sup>	Unnotch <sup>c</sup>	
No glass	13,800	3.5	7,600	3.5	0.7	8.4	158(70)
Virgin roving	16,000	9.6	9,300	11.2	0.7	5.2	394(201)
Commercial No. 1	30,700	11.3	19,100	12.2	2.1	13.8	428(220)
Commercial No. 2	30,300	10.3	18,500	11.7	2.1	12.7	426(219)
Commercial No. 3	28,900	9.5	18,700	12.5	2.4	12.8	430(221)
A-1100	23,600	10.5	14,200	11.9	0.9	7.5	405(207)
A-186	22,200	10.6	24,300	12.0	1.3	8.9	412(211)
A-187	24,700	10.2	14,400	11.7	1.4	9.6	415(213)

<sup>a</sup>Celanese J-105 thermoplastic polyester, poly(butylene terephthalate) with 30% glass.

<sup>b</sup>Ft × lb/inch of notch.

<sup>c</sup>Ft × lb/inch of width.

<sup>d</sup>At 264 psi.

**Table 12b. Wet Strength Retention of Glass-Reinforced PBT.**

Size	Tensile Strength, psi					Tensile Modulus, psi $\times 10^5$		
	Dry	16 hr Wet <sup>a</sup>	% Ret.	One-Week Boil <sup>b</sup>	% Ret.	Dry	16 hr Wet <sup>a</sup>	One-Week Boil <sup>b</sup>
No glass	7,600	7,500	99	1,700	23	3.5	2.8	3.0
Virgin roving	9,300	8,400	90	3,000	33	11.2	8.3	7.0
Commercial No. 1	19,100	18,500	97	9,500	50	12.2	11.6	10.4
Commercial No. 2	18,500	18,000	97	12,200	66	11.7	11.8	10.5
Commercial No. 3	18,700	17,700	95	10,300	55	12.5	12.1	10.0
A-1100	14,200	13,100	92	6,600	47	11.9	10.3	8.5
A-186	14,300	12,900	90	5,200	36	12.0	11.3	8.5
A-187	14,400	13,800	96	6,000	42	11.7	11.6	8.7

<sup>a</sup>16 hr in 50°C water.<sup>b</sup>One week in 100°C water.**Table 13a. Dry Physicals of Reinforced Polypropylene.<sup>a</sup>**

Size	Flexural Strength psi	Flexural Modulus, psi $\times 10^5$	Tensile Strength, psi	Tensile Modulus, psi $\times 10^5$	Izod Impact Strength		Heat-Distortion Temperature, <sup>d</sup> °F(°C)
					Notch <sup>b</sup>	Unnotch <sup>c</sup>	
No glass	6,600	1.5	4,500	2.2	0.5	14.5	142(61)
Virgin roving	8,100	5.3	4,900	9.5	0.9	5.0	246(119)
Commercial No. 1	13,800	4.8	8,300	8.5	3.3	7.7	306(152)
Commercial No. 2	10,500	5.2	6,600	8.1	2.6	6.1	298(148)
Commercial No. 3	12,100	4.9	7,600	7.9	3.7	8.0	280(138)
A-1100	9,900	4.8	5,600	8.8	1.9	5.3	280(138)
A-174	10,900	5.3	6,000	8.8	2.5	6.7	295(146)

<sup>a</sup>Hercules Pro-Fax 6523 premix with 30 wt% chopped glass strand.<sup>b</sup>In ft  $\times$  lb/inch of notch.<sup>c</sup>In ft  $\times$  lb/inch of width.<sup>d</sup>At 264 psi.**Table 13b. Wet Physicals of Reinforced Polypropylene.<sup>a</sup>**

Size	Tensile Strength, psi		% Ret.	Tensile Modulus, psi $\times 10^5$	
	Dry	Wet <sup>b</sup>		Dry	Wet <sup>b</sup>
No glass	4,500	4,300	96	2.2	1.9
Virgin roving	4,900	4,300	88	9.5	5.5
Commercial No. 1	8,300	7,200	87	8.5	6.6
Commercial No. 2	6,600	6,100	92	8.1	6.6
Commercial No. 3	7,600	7,200	95	7.9	7.0
A-1100	5,600	5,000	89	8.8	5.8
A-174	6,000	5,400	90	8.8	7.4

<sup>a</sup>Hercules Pro-Fax 6523 premix with 30 wt% chopped glass strand.<sup>b</sup>After boiling for 24 hr.

**Table 14. 50% Mica<sup>a</sup> Filled Polypropylene<sup>b</sup> Composites.**

	<i>Without Additives</i>	<i>With UCARSIL PC-1A/PC-1B<sup>c</sup></i>
Tensile strength, psi	4,300	7,070
Tan. flexural modulus, psi $\times 10^3$	1,430	1,210
Flexural strength, psi	7,400	10,600
Notched Izod impact strength, ft-lb/in.	0.13	0.20

<sup>a</sup>Grade 200 HK, Marietta Resources, Ltd.<sup>b</sup>Pro-Fax 6523 PM Powder, Hercules, Inc.<sup>c</sup>Total 1.25% based on total composite, 4/1 ratio.**Table 15. 50% Mica<sup>a</sup> Filled High Density Polyethylene<sup>b</sup> Composites.**

	<i>Without Additives</i>	<i>With UCARSIL PC-1A/PC-1B<sup>c</sup></i>
Tensile strength, psi	3,510	5,530
Tan. flexural modulus, psi $\times 10^3$	510	590
Flexural strength, psi	5,080	7,260
Notched Izod impact strength, ft-lb/in.	0.23	0.27

<sup>a</sup>Grade 200 HK, Marietta Resources, Ltd.<sup>b</sup>G-7006, Union Carbide Corp.<sup>c</sup>Total 1.5% based on total composite, 2/1 ratio.**Table 16. 30% Fiberglass<sup>a</sup> Reinforced Homopolymer PP.<sup>b</sup>**

	<i>Composite Properties</i>	
	<i>Without OSC<sup>c</sup></i>	<i>With 2% UCARSIL PC-1A/PC-1B<sup>d</sup> (3/1 ratio)</i>
Tensile strength, psi	6,140	8,850
Flexural modulus, tan., psi $\times 10^3$	750	750
Flexural strength, psi	9,100	12,600
Notched Izod impact strength, ft-lb/in.	1.5	1.4
Unnotched Izod impact strength, ft-lb/in.	3.2	4.3

<sup>a</sup>OCF-885BD (3/16 in.).<sup>b</sup>PRO-FAX 6523.<sup>c</sup>Organosilicon chemicals.<sup>d</sup>Integrally blended.

Godlewski<sup>16</sup> has reported that the use of two new materials, Union Carbide FR-1A and FR-1B (proprietary compositions) permit easier incorporation of high levels of ATH into HDPE and to significantly enhance composite properties as shown in Table 17.

## Elastomers

Mineral filled elastomers are not usually considered to be composite materials, although they have many of the characteristics common to composites. Chief among these is the exis-

**Table 17. Property Enhancement in a 65% ATH<sup>a</sup>/HDPE<sup>b</sup> Composite.**

	<i>Unfilled HDPE</i>	<i>65% ATH Composites</i>	
		<i>Without UCARSIL FR-1A/FR-1B</i>	<i>With UCARSIL FR-1A/FR-1B<sup>c</sup></i>
Tensile strength, psi	3,080	2,750	4,750
Flexural strength, psi	3,250	3,850	6,050
Tan. flexural modulus, psi $\times 10^3$	150	320	350
Gardner Impact strength, in.-lb/in.	—	10	200
Unnotched Izod impact strength, ft-lb/in.	—	2	14

<sup>a</sup>Alcoa Hydral 710.<sup>b</sup>G-7030 From UCC.<sup>c</sup>UCARSIL FR-1A/FR-1B (1/1 ratio) 2% based on ATH amount.

tence of a large interfacial area between the continuous organic polymer phase and the discontinuous dispersed mineral phase. It is well known that poor wetting of a filler by a polymer is manifested by vacuole formation in a stressed system at a low level of stored energy. These vacuoles often act as stress concentrators and catastrophic failure occurs at much lower levels of stored energy than would be the case for a well wetted or bonded system. As has been discussed for the case of thermosetting and thermoplastic resins, this interface can be effectively bridged by the use of a silane coupling agent selected to participate in the cure chemistry of the specific elastomer. Ranney and Pagano<sup>17</sup> studied the relationship between silane functionality and resultant elastomer properties in a mineral filled EPDM system. Table 18 summarizes their results.

Clearly, the use of saturated aliphatic silanes such as the amyl (A-16, amyltriethoxysilane) and methyl (A-162, methyltriethoxysilane), substituted products is largely ineffective due to lack of reactivity in this free radical system. The rather small increase in tensile properties observed may be ascribed to improved filler-elastomer wetting.

The organofunctional coupling agents all give very significant improvements in modulus and tensile, but to different degrees, depending on their relative reactivity in this peroxide cured system. The methacryloxypropyltrimethoxysilane (A-174) is considerably more effective than vinylsilane (A-172), as could be predicted from the relative reactivity of the double bond moiety. The  $\gamma$ -mercaptopropyltrimethoxysilane (A-189), capable of chain transfer reac-

tions, is relatively effective in improving the modulus and tensile properties. The  $\gamma$ -amino-propyltriethoxysilane (A-1100) also provides a high level of filler-elastomer interfacial bonding, as evidenced by the physical property data.

In addition to the low physical properties shown by the mineral filled elastomer without silane in Table 18, two other factors have limited the use of mineral fillers. These are heat buildup in flexing (likely related to poor wetting of the filler by the elastomer) and poor abrasion resistance, particularly as it relates to road wear. Wagner<sup>18</sup> has studied the effect of a mercapto-functional silane (A-189) on these properties and compared the results to those obtained using a carbon (HAF) black filler. Table 19 summarizes his results.

As would be expected, the mercaptosilane increases the modulus and tensile to values comparable to those of the carbon black compound. In the Goodrich flexometer test, the heat buildup, which is known to be a rather severe problem, is 27°C, which is well below the value obtained with carbon black. The mercaptosilane also improves the compression set and the Pico Abrasion Index. Significantly, the Road Wear Index was improved to give equivalency to the carbon black compound.

At present, a large area of interest in silane coupling agents in elastomers is in wire and cable applications.<sup>19</sup> The electrical properties of white filled EPM and EPDM cables deteriorate rapidly under conditions of high humidity, due to adsorption of water at the filler/rubber interface. The use of silanes prevents water ingress and maintains the electrical properties. Table 20 shows the effect of various silanes on the

**Table 18. Effect of Organofunctionality of Silane Coupling Agent on Physical Properties of Peroxide-Cured EPDM.**

<i>Silane Monomer</i>	<i>Properties</i>	
	<i>300% Modulus psi</i>	<i>Tensile Strength, psi</i>
Control, no silane	420	895
Amyl (A-16)	410	995
Methyl (A-162)	500	1,050
Vinyl (A-172)	1,110	1,380
Mercapto (A-189)	1,200	1,540
Amino (A-1100)	1,440	1,640
Methacryloxy (A-174)	1,660	1,660

**Table 19. Effect of Mercaptosilane Coupling Agent on a Silica-Filled SBR Compound.**

SBR 1502	100	100	100
Hi-Sil 233	60	60	—
N-285 Black	—	—	60
Mercaptosilane A-189	—	1.5	—
300% modulus, psi	725	1980	2220
Tensile, psi	2680	3760	3520
Elongation, %	580	460	460
Hardness	71	67	74
Goodrich flexometer $\Delta T$ , °C	47	27	41
Compression set, % (B)	25	12	20
Pico abrasion index, %	81	131	170
Road wear index	79	114	110

**Table 20. Electrical Properties of Hard Clay Filled EPDM Compounds Containing a Silane Coupling Agent.**

	Silane				
	None	A-172	A-174	A-189	A-1100
S.I.C. (specific inductive capacitance), kC/sec					
Unaged	2.91	3.00	2.91	2.93	2.94
7 days	6.08	3.35	3.30	3.53	5.04
14 days	6.84	3.58	3.31	3.69	5.57
Dissipation Factor, sec/cycle-ohm-farad					
Unaged	0.009	0.008	0.005	0.007	0.007
7 days	0.182	0.025	0.017	0.024	0.101
14 days	0.188	0.024	0.018	0.024	0.100

electrical properties of a clay filled EPM compound.

Silane coupling agents are now used with mineral fillers in passenger tires (tread stock, carcass, and sidewall), off-the-road tires, engine mounts, and in many specialty applications such as conveyor belts, gaskets, ignition wire, hose compounds and solid golf balls. While the automotive segment employing SBR, natural, and butyl rubber represents the largest market segment, the combination of the mercapto- or aminosilane with a mineral filler in nitrile, neoprene, EPDM, and other specialty elastomers has provided a new and exciting formulation technique for obtaining high performance elastomeric products.

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# Non-Silane Coupling Agents

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Surface treatment of substrates has been an important factor in obtaining well bonded structures. Modifying or treating the substrate surface is usually essential for achieving a bond that will survive long term stress and exposure to environmental conditions. In composites technology, the term *coupling agents* has been used to designate chemicals that are used to treat the surface of fillers and reinforcements in order to obtain optimum physical properties and for long-term retention of physical properties. Coupling agents are chemical molecules with dual functionality, wherein one part of the molecule will adhere to one surface, e.g., filler or reinforcement, while another part of the molecule provides a bond to the other material, e.g., the polymer matrix. Thus, a bonded bridge is formed between two different materials.

Coupling agents have usually been applied by two different methods. The first and predominant method has been the application of the coupling agent to the surface of the filler or reinforcement. Typically, this has been accomplished by treating the filler or reinforcement with a dilute solution of the coupling agent, then evaporating the solvent. The objective is to obtain a controlled and uniform thin coating or monomolecular film of the coupling agent onto the treated surface. Application levels have usually ranged between 0.1% and 1% by weight of the treated material. The second method, the *integral blend* procedure, involves the addition to the resin of about 1–2% of cou-

pling agent by weight of the material to be treated. The performance of this method will depend upon the extent to which the coupling agent will migrate to the interface during later processing of the composite.

Coupling agents can provide benefits as processing aids for polymer matrix composites. Dramatic reductions in viscosity can occur in some highly filled liquid polymers when a relatively small quantity of an appropriate coupling agent is added to the formulation.

Silanes are currently the predominant coupling agents, and these materials have been presented in another chapter of this Handbook. The following sections will review non-silane materials that are being used as coupling agents to improve the processing and properties of polymer matrix composites.

## TITANATES/ZIRCONATES

Titanates and zirconates produced by Kenrich Petrochemicals, Inc. have received much attention in recent years, and show promise of affording some remarkable improvements in processing characteristics and final properties of many composite systems.<sup>1</sup>

Typical generalized structures of titanate and zirconate coupling agents are shown in Fig. 1. One of the proposed mechanisms for the effectiveness of the titanates in some composite systems is shown in Fig. 2. The water of hydration at the inorganic filler or fiber surface is re-

Properties of Titanate/Zirconate Coupling Agents		
Titanate or Zirconate Type	Applications/Advantages	Chemical Structure
Monoalkoxy Titanate	Stearic Acid Functionality; Aids Dispersion of Mineral Fillers in Polyolefins	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{CH}-\text{O}-\text{Ti}(\text{O}-\text{P}(\text{OH})(\text{O}-\text{P}(\text{OC}_6\text{H}_{17})_2)_2 \end{array}$
Chelate Titanate	Greater Stability in Wet Environments	$\begin{array}{c} \text{O} \quad \text{O} \quad \text{O} \\    \quad    \quad    \\ \text{C}-\text{O}-\text{Ti}(\text{O}-\text{P}-\text{O}-\text{P}(\text{OC}_6\text{H}_{17})_2)_2 \\   \quad   \\ \text{CH}_2-\text{O} \quad \text{OH} \end{array}$
Quat Titanate	Water Soluble	$\begin{array}{c} \text{O} \quad \text{O} \quad \text{O} \\    \quad    \quad    \\ \text{C}-\text{O}-\text{Ti}(\text{O}-\text{P}-\text{O}-\text{P}(\text{OC}_6\text{H}_{17})_2)_2 \\   \quad   \quad   \\ \text{CH}_2-\text{O} \quad \text{H} \quad \text{O}^+ \\ \quad \quad   \quad   \\ \quad \quad \text{R}-\text{N}-\text{R} \end{array}$
Coordinate Titanate	Phosphite Functionality; Reduces Epoxy Viscosity w/o Accelerating Cure	$(\text{RO})_2\text{Ti} \cdot (\text{HP}(\text{OC}_6\text{H}_{17})_2)_2$ $\begin{array}{c} \text{O} \\    \\ \text{P} \end{array}$
Neoalkoxy Titanate	Eliminates Pretreatment Associated with High Temperature Thermoplastics and Polyurethanes	$\text{R}^+-\text{O}-\text{Ti}(\text{O}-\text{P}(\text{OH})(\text{O}-\text{P}(\text{OC}_6\text{H}_{17})_2)_2$
Neoalkoxy Zirconate	Accelerates Peroxide- and Air-based Cures; e.g., Polyester SMC/BMC	$\text{R}^+-\text{O}-\text{Zr}(\text{O}-\text{P}(\text{OH})(\text{O}-\text{P}(\text{OC}_6\text{H}_{17})_2)_2$
Cycloheteroatom Titanate	Ultra-high Thermal Properties for Specialty Applications	$\begin{array}{c} \text{O} \quad \text{O} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{Ti} \quad \text{O} \quad \text{O} \quad \text{R} \end{array}$

Fig. 1. Typical generalized structures of titanate/zirconate coupling agents. (Courtesy Kenrich Petrochemicals, Inc.)

placed with a monomolecular layer of organo-functional titanate. This improved wetting at the inorganic/organic interface increases the degree of displacement of interstitial air by the organic matrix. Dispersion tests by Kenrich showed that 0.5% titanate coupling agent by weight on calcium carbonate reduced the viscosity of a 50% calcium carbonate filled dioctyl phthalate from 177,000 cps to 2,600 cps. Fig. 3 shows that 1% by weight addition of titanate to  $\text{TiO}_2$  changed a 40% dioctyl phthalate system from a nonflowing viscosity to a very fluid state.

Use of organometallic coupling agents (additives) as process aids, adhesion promoters, and physical property enhancers in a wide va-

riety of polymer disciplines is well documented in the literature<sup>1-4</sup> and in a Reference Manual published by Kenrich.

Improved bonding of fiberglass, Kevlar, and carbon fiber to a variety of elastomeric, epoxy, and peroxide cured unsaturated thermoset substrates has been achieved by including minor proportions of organotitanate or organozirconate coupling agents in various polymer matrices.<sup>2</sup> The addition of 0.2% LZ 97, which is a Kenrich zirconium (IV) neoalkenolato-*tris*(3-amino)phenylato compound, to an anhydride-cured epoxy/fiberglass pipe results in a dramatic increase in interfacial adhesion. Fig. 4 shows that a control without the LZ 97 has the fiberglass strands evident within the composite,

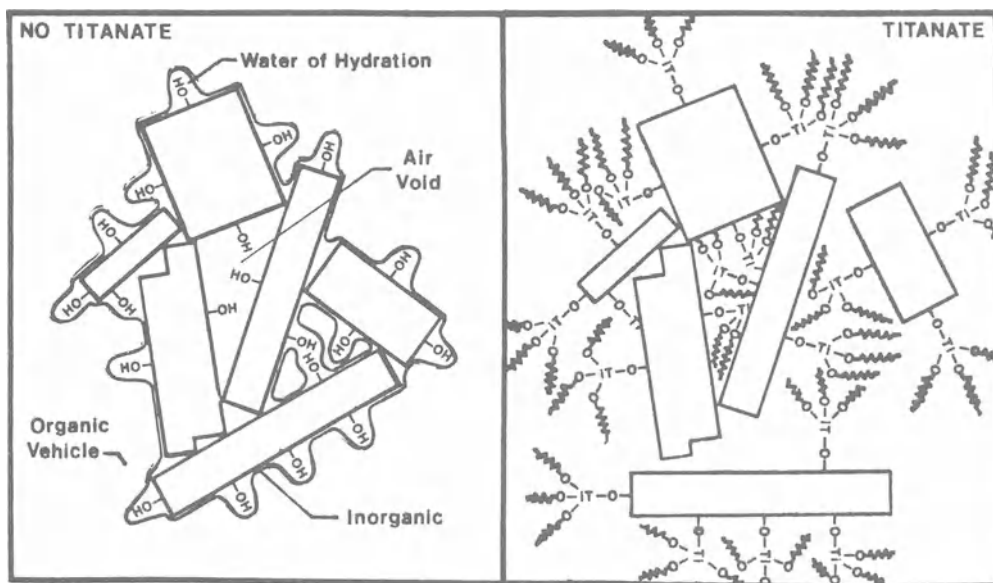


Fig. 2. The proposed mechanism for deposition of a monolayer of triorganofunctional titanate to effect the elimination of inorganic water of hydration and air voids resulting in deagglomeration. (Courtesy Kenrich Petrochemicals, Inc.)

whereas the addition of the titanate provides an improvement in interface adhesion that eliminates the appearance of separate glass fibers.

The enhancement of adhesion provided by asymmetric organotitanates and zirconates in reinforced composites appears to be a consequence of the interaction of multiple mechanisms, including ligand-specific interfacial wetting enhancement, primary chemical bond formation between the substrate particulate and resin matrix, and, in many instances, matrix re-polymerization and reinforcement surface modification. The particular mechanism which is dominant in a specific application appears to

be system dependent. For example, the enhancement of processability effected by the coupling agent appears to be the primary basis for the upgrade in properties observed in  $\text{CaCO}_3$  filled polyolefins, whereas the improved mechanical properties by use of amino zirconates in glass filled nylon appears to be primarily a result of the bonding of the coupling agent to the glass surface and the resin matrix.<sup>3</sup>

Monte and Sugerman<sup>3</sup> have shown specific organotitanium/organozirconium derived coupling agents as being effective especially in improving the impact strength in composites as widely disparate as  $\text{CaCO}_3$  filled polypropylene and polyvinyl chloride, glass filled polyurethane, and Kevlar reinforced epoxy.

The organotitanate and organozirconate coupling agents and their analogs have been effective in promoting adhesion between various components of polymer laminates and laminates/coatings to metallic and inorganic surfaces.

Kenrich is the outstanding company that has conducted research on titanate and zirconate coupling agents and produced these materials for adhesives and composites. This effort has led to many patents related to their products. U.S. Patent, 4,600,789 (July 15, 1986) and

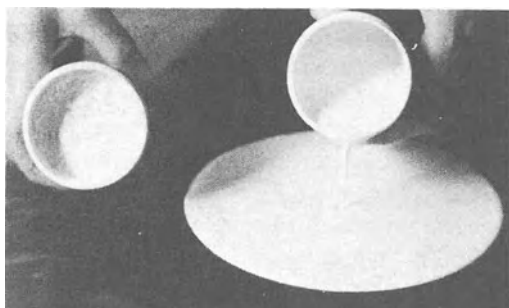


Fig. 3. The addition of 1 wt% of titanate in a 40%  $\text{TiO}_2$ /DOP dispersion creates a remarkable change in viscosity. The material at left has no titanate. (Courtesy Kenrich Petrochemicals, Inc.)



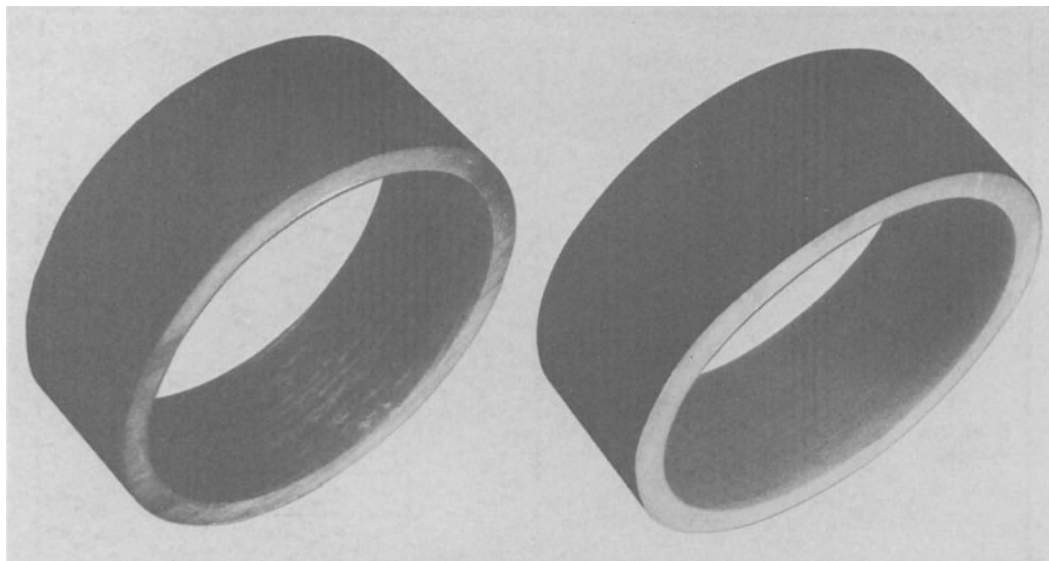


Fig. 4. Fiberglass wound epoxy pipe. The control on the left shows the fiberglass windings projecting through the anhydride-cured epoxy pipe wall. The sample on the right, containing 0.2% LZ 97 has the same degree of fiberglass reinforcement, but shows no apparent fiberglass because of almost complete interfacial adhesion of epoxy to reinforcement.

4,623,738 (November 18, 1986) were granted to G. Sugerman and S. J. Monte of Kenrich for a new generation of neopositioned quaternary carbon type (neoalkoxy) coupling agents which exhibit novel thermal stability—even when introduced into unfilled polymers at 400°C.

Dupont has a line of organic titanates, TY-ZOR TPT, TBT, and TOT, that can be used to modify surfaces so that they are oleophilic or hydrophilic. These products are dispersion aids and promote dispersion of pigments in resins and paints. They modify surfaces to make them more compatible with adhesives and thereby promote adhesion.

## ZIRCOALUMINATES

Zircoaluminates or aluminum zirconium metallo-organic complexes have proven useful as coupling agents and adhesion promoters.

On September 3, 1985, two patents were granted to L. B. Cohen, assigned to Cavedon Chemical Co., Inc., Woonsocket, R.I.: U.S. Patent 4,539,048 and 4,539,049, describing aluminum zirconium metalloorganic complexes “useful as coupling agents.” These complexes “chemically modify the surface of

fibrous and particulate inorganic substances and certain organic particulates, thereby resulting in hydrophobic, organophilic fibers and particles having improved rheological properties which facilitate higher filler or fiber loading levels,” e.g., in fiberglass-reinforced polyester laminates. Laminate performance was equivalent to that obtained with a methacrylate silane coupling agent and superior to methacrylate chromic chloride. According to Cohen’s U.S. Patent 4,764,632 (August 16, 1988), multifunctional amino zircoaluminates are effective as high temperature adhesion promoters.

Zircoaluminate coupling agents are analogous to the silanes. Each of their product line has organic functionality and an inorganic backbone, so that one end can interact with the matrix resin and the inorganic component will have an affinity for the filler or reinforcement surface.

A representative structure of this type of material is shown in Fig. 5. Cavedon line (Table 1) includes amino, carboxy, oleophilic, methacryloxy, and mercapto functionality.

The potential of this line of coupling agents has been described in a number of publications.<sup>5-9</sup>

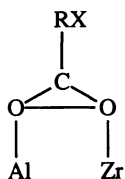


Fig. 5. Representative structure of zircoaluminate coupling agents. RX is an organofunctional group.

### Cavco Mod Adhesive Applications

Cavco Mod CPM has been used in a blue polyamide ink to enhance adhesion to untreated polyethylene. This is a first report indicating that the conventional process of corona discharge of PE, PP and polyester film may be obviated by use of Cavco Mod.

Cavco Mod APG has been used to improve the bond of epoxy adhesives for both metallic and nonmetallic substrates. It has been used in  $\text{CaCO}_3$ /Epoxy to reduce viscosity and promote adhesion to a variety of substrates. It has also been used in an adhesive, which was described in U.S. Patent 4,690,966 (L. B. Cohen, 1986), to enhance bonding between rubber and metal substrates.

Cavco Mod C has been used in a phenolic primer to promote adhesion of a rubber-based coating to steel.

## MISCELLANEOUS COUPLING AGENTS

### Chrome Complexes

Among the first commercial products used as coupling agents for glass filaments was the Vo-

lan line marketed by DuPont. These materials are coordination complexes of carboxylic acids with trivalent chromium chlorides. Volan is usually applied to glass fabric by a specific treating and washing step, known in the industry as the "A" finish. This finish was qualified under military specification MIL-F-9118A, October 11, 1954, and was the standard finish for glass filament reinforcements for many years. However, its use tapered off when the silanes proved to offer better performance, especially with regard to water resistance. A test that was frequently used for accelerated determination of long-term resistance to water was to expose the fiberglass laminate for 2 hours in boiling water. In this simple test, a laminate containing glass filaments without a coupling agent will exhibit great loss of flexural strength, in the order of about 40%. The Volan A treatment will provide good retention of flexural strength in this test; however, properly selected silanes will provide excellent retention of the flexural strength.

The Chemical Abstracts Index name for the prime component of Volan is *methacrylato chromic chloride hydroxide*. The CAS Registry Number is 15096-41-0. The structure is shown in Fig. 6.

### Polymer Additives

There are polymer additives that can serve the function of coupling agents.<sup>10</sup> *Acrylic acid-modified polypropylene* has been used to improve the properties of filled and reinforced polypropylene compounds. Fig. 7 shows the improvement in tensile strength that is obtained

Table 1. Cavedon Zircoaluminates.

Functionality	Cavco Mod Products	Recommended Resins
Amino	A APG	Epoxy, nylon, phenolic, urethane, furan, melamine, PVC
Carboxy	C, C-1 CPM, CPG, C-1PM	Polybutylene terephthalate, Acrylics, SBR
Oleophilic	F FPM	PE, PP, polybutadiene
Methacryloxy	M	Unsaturated polyesters,
Methacryloxy/oleophilic	M-1 MPM, MPG, M-1PM	PE, PP, polybutadiene, ABS
Mercapto	S SPM	NBR, SBR, EPDM, neoprene

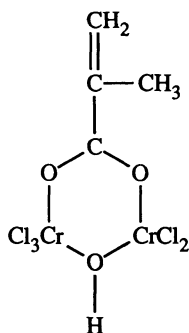


Fig. 6. Methacrylato chromic chloride.

when acrylic acid-modified polypropylene is added to a mica-filled polypropylene.

BP Performance Polymers, Inc., Hackettstown, N.J. has several grades of polypropylene that have been grafted with acrylic acid. This modified polypropylene has provided improved bonding to mica, talc, and glass fiber in polypropylene composites.

*Copolymers of styrene and maleic anhydride* are produced by Sartomer Company under the trade name SMA resins. Grades 1000, 2000, and 3000 are unmodified copolymers with styrene-maleic anhydride ratios of 1:1, 2:1, and

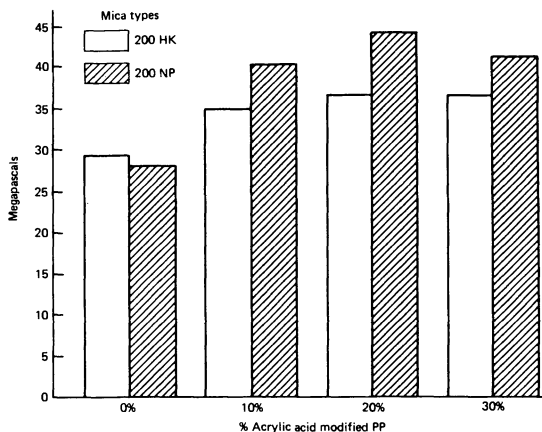


Fig. 7. Acid-modified polypropylene/mica composite. Acid-modified PP raises tensile strength of PP filled with untreated mica (200 HK) to a higher level than with more expensive surface-treated mica (200 NP) and no added coupling agent.

3:1 respectively. They have been shown to provide improved adhesion, better dispersion, reduced viscosity, and improved mechanical properties in filled and reinforced thermoplastic composites. Fig. 8 shows the structure of the SMA resins. Table 2 shows the improvement in tensile strength and tensile modulus that results from the addition of SMA resin to a polypropylene/clay composite.

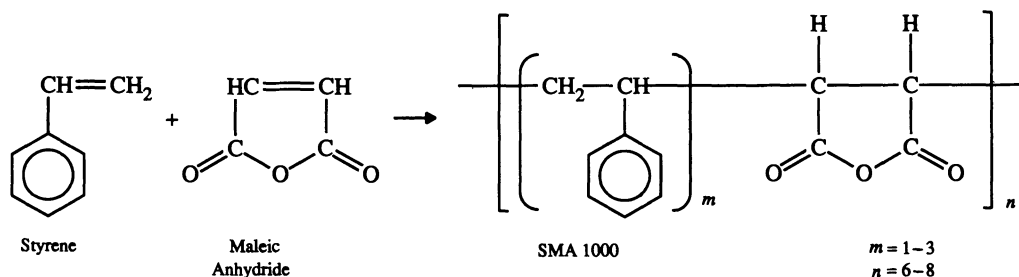


Fig. 8. SMA resins.

Table 2. Effect of SMA Resin on Polypropylene/Clay Composites.

Composite <sup>a</sup> PP/ Clay <sup>b</sup> /SMA Resin	Tensile Strength, psi		Flex Modulus, psi	Ult. Elongation, %
	Yield	Break		
70/30/0	— <sup>c</sup>	3340	374,000	4.6
70/30/1.3 SMA 1000	4280	4020	423,000	4.4
70/30/1.3 SMA 2000	4060	3600	426,000	5.3
70/30/1.3 SMA 3000	4270	4160	451,000	4.1

<sup>a</sup>Composites prepared by dilution with virgin PP of 70/30 Clay/PP concentrates containing 3.0 parts SMA resin.

<sup>b</sup>Hydrite 10 (Georgia Kaolin Co.).

<sup>c</sup>No yield.

**Table 3. T-Peel Strength of SMA Resin Modified Polyethylene.**

Substrate	SMA Resin, wt %	T-Peel, lb/in.	
		Aluminum	Steel
LDPE <sup>a</sup>	—	0.1	0.3
LDPE <sup>a</sup>	1000 (10)	0.2	0.6–1.6
LDPE <sup>a</sup>	3000 (10)	0.1–2.3	0.5–2.8
LDPE <sup>b</sup>	—	0.3	0.2
LDPE <sup>b</sup>	1000 (10)	4.1–5.3	3.7
LDPE <sup>b</sup>	3000 (10)	0.2	0.4

<sup>a</sup>Dylan 2020F (ARCO Polymers, Inc.).<sup>b</sup>Super Dylan SDP 640 (ARCO Polymers, Inc.).

SMA resin modified polyethylenes were compared to unmodified resins in adhesion to aluminum and steel. Table 3 indicates that adhesion is significantly improved by the addition of about 10% of the appropriate SMA resin.

### Fluorosurfactants

DuPont produces a line of fluorosurfactants, tradenamed Zonyl, that have been recommended for use as a resin additive for improved wetting and bonding with fillers.

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# Resins for Elastomer-Based Adhesives

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Elastomer-based adhesives are widely used in industrial and household applications. Pressure sensitive tapes and labels, hot melt packaging adhesives, disposable products, construction adhesives, and hot melt bookbinding adhesives are just a few of the adhesive systems which have shown rapid market growth in recent years. Other types of elastomer-based adhesives have been developed for high-strength structural applications required by the aircraft, automotive, and construction industries. The wide range of properties available in these adhesive systems is due in part to: (a) the variety of properties obtainable in natural and synthetic elastomers and (b) the many modifying materials such as tackifying resins, reinforcing resins, fillers, plasticizers, and curing agents which may be incorporated into the adhesive formulation.

## HISTORICAL BACKGROUND

The earliest rubber adhesives were merely simple solutions of unmodified natural rubber. The adhesive properties of raw natural rubber were recognized as long ago as 1791, when naphtha

solutions of rubber were used for laminating and waterproofing textile products. Later, such adhesives were vulcanized after application. Adhesives made with natural rubber latex were first prepared in the middle of the 19th Century. The early solvent cements were seldom formulated with resins, although the inclusion of rosin was found to be beneficial. Strength requirements in these early adhesives were, for the most part, low.

With the development of synthetic elastomers during World War II, new types of adhesives appeared for application to a broader range of substrates and for use at higher temperatures. Styrene-butadiene and butadiene-acrylonitrile copolymers found application in new adhesives. There were also significant concurrent developments in adhesives based on chlorinated rubber, polychloroprene (neoprene), and polysulfide rubber. Development of carboxylic elastomers, silicone rubbers, and polyurethanes followed.

The introduction of a number of elastomer-thermosetting resin blends extended the application of elastomer-based adhesives to structural applications. These blends typically

consisted of reactive phenolic resins with neoprene or nitrile rubber. The key properties of these adhesives were high strength and low creep.

The commercial introduction of the thermoplastic block copolymers in 1965 gave impetus to the development of high performance pressure sensitive and hot melt adhesives. These unique materials, based on styrene endblocks and either isoprene, butadiene, or ethylene-butylene midblocks, have become established as the elastomer of choice in some of the fastest growing segments of the adhesive and sealant industry.

## ADHESIVE COMPONENTS

Elastomer-based adhesives typically contain an elastomer and a tackifying or modifying resin as key components. A number of other ingredients may be included:

1. Elastomer.
2. Tackifying (modifying) resin.
3. Plasticizer or softener.
4. Fillers.
5. Pigments.
6. Curing agents.
7. Antioxidants.

An elastomer is a natural or synthetic polymer with rubberlike properties. These materials exhibit high extensibility and quick, forceful recovery. Examples of elastomers used in adhesive applications are:

- Natural rubber.
- Acrylic copolymers.
- Styrenic block copolymers.
- Butyl rubber.
- Chlorinated rubber.
- Polyisobutylene.
- Styrene-butadiene rubber (SBT).
- Polychloroprene (neoprene).
- Silicone rubber.
- Ethylene-propylene copolymer rubber.
- Polyurethanes.
- EPDM.

The tackifying (or modifying) resins which are used in formulating elastomer-based adhesives are obtained by the polymerization of petroleum and terpene feedstreams, as well as

from the derivatization of wood, gum, and tall oil rosin. These are low molecular weight resins, with the  $M_w$  seldom exceeding 2000 and often below 1000. In addition, thermoplastic and thermosetting phenolic resins are often incorporated into high performance adhesives. Tackifying resins comprise the subject matter for most of this chapter and will be discussed in detail later.

Plasticizers and softeners include the phthalates such as dioctyl phthalate and diisobutyl phthalate, natural oils such as lanolin, and paraffin, naphthenic and aromatic oils obtained from petroleum refining. Liquid resins from rosin or petroleum feedstocks can serve the dual purpose of tackification and plasticization.

Fillers are materials such as carbon black, zinc oxide, clays, chalk, whittings, calcium silicate, and barium sulfate. These materials are used to reduce cost, increase hardness, improve abrasion resistance, and to modify the cohesive strength of the formulation.

Curing agents are incorporated into the adhesive formulation to increase the cohesive strength of the elastomer. Sulfur was the most commonly used curing agent in early natural rubber adhesive systems, but it has been largely replaced by organic peroxides and isocyanate crosslinking systems.

The antioxidants used in adhesive formulations are similar to those used in rubber compounding and include materials such as the aromatic amines, substituted phenols, and hydroquinones. Elastomer and resin manufacturers typically incorporate antioxidants (0.1–0.3 wt %) in their products for protection during storage and shipment. Adhesive formulators will usually add additional antioxidant to protect the adhesive during processing and use. It is not unusual for an adhesive formulation to contain as many as three or four different types of antioxidants.

In addition to the components cited above, aqueous adhesives based on rubber latexes and resin emulsions also employ a wide variety of materials, such as protective colloids, emulsifiers, thickeners, and emulsion stabilizers. The primary function of these additives is to provide stability to the aqueous adhesive. They do not necessarily enhance the adhesive properties of the finished composition. In fact, a careful

compromise must be reached between the dispersion properties and the performance characteristics of the adhesive. Migration of stabilizers can reduce the tack of pressure sensitive adhesives upon aging or can cause staining of backing substrates. Improper use of stabilizers in latex adhesives can also result in poor resistance to moisture in the final application.

## TYPES OF ELASTOMER-BASED ADHESIVES

Pressure sensitive adhesives based on a variety of elastomers and applied from either latex, solvent, or hot melt systems have shown rapid growth in recent years. In addition, the development of hot melt assembly adhesives based on the styrenic thermoplastic elastomers is a key factor in the production of disposable diapers and other sanitary products. Even though the current emphasis of elastomer-based adhesive development is on pressure sensitive adhesives, large volumes of solvent cements, latex cements, and mastics are still produced.

### Solvent Cements

The preparation of many solvent cements, mastics, and pressure sensitive adhesives involves milling or mastication of natural rubber. The elastomer, obtained by the coagulation of natural rubber latex, is usually kneaded by passing repeatedly between two steel rolls moving at different speeds or in a Banbury-type mixer, usually at an elevated temperature. The polymer is subjected to compression followed by strong shearing forces. The very high shearing force mechanically ruptures the elastomer chains, thus reducing the molecular weight of the rubber. Whereas the starting material was essentially elastic and capable of undergoing permanent deformation only under extreme loads, after milling, it becomes softer, readily deformable, and soluble in both aliphatic and aromatic solvents.

In practice, it is difficult to define and control rubber milling conditions. The concentration and type of natural products in raw natural rubber vary, as do the amount and type of materials in the synthetic rubbers. These variables influence the result of mastication. The milling

operation itself is one of skill and art. Temperature, speed of rolls, surrounding atmosphere, time of milling, and clearance between the rolls are all variables which are difficult to duplicate, not only from machine to machine, but for each batch operation on the same machine. The ability to mill to the same level of degradation is essential to obtaining a consistent cohesive strength in the adhesive formulation. Differences in milling levels become especially apparent in the shear resistance of natural rubber pressure sensitive adhesive unless the cohesive strength is regenerated by curing of the adhesive.

The measurement of the effects of mastication on the molecular weight of the rubber can be time-consuming even with sophisticated techniques such as size exclusion chromatography. The viscosity of natural rubber is usually measured by means of a Mooney rotating disk viscometer,<sup>1</sup> an established method for following the effect of mill time and conditions. Adhesive formulators have successfully used this instrument to correlate Mooney viscosity to rubber end-use properties.

Solvent cements are generally produced by removing the milled elastomer from the mill and dissolving it in solvent. This "cutting" of the rubber into a solvent is accomplished in low-speed mixing equipment known as *churns* or in a variety of high-speed, heavy-duty mixers. For natural rubber and SBR, solvents such as toluene, hexane, or naphtha are commonly used. For nitrile, neoprene, and other polar polymers, polar solvents such as methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), or chlorinated solvents may be used, alone or in blends with the nonpolar solvents. The blend of solvents finally used by the adhesive producer will depend not only on solvent power, but on the relative rates of evaporation which control drying time. The dissolved rubber can then be blended with whatever additives are needed to obtain the desired adhesive performance.

The process of masticating and dissolving natural rubber is important for pressure sensitive formulation as well as for solvent cement production. Pressure sensitive tapes and labels based on natural rubber are a significant part of the rapidly growing pressure sensitive adhesive

industry and will be discussed in more detail later.

Solvent cements are usually supplied at concentrations of 10–25% solids, with viscosities in the range of 1,000–30,000 cPs. They may be applied by brush, spray, doctor blade, reverse-roll coater, hand roller, trowel, and many other application methods. The proper coating of the adhesive is obtained by establishing the correct viscosity for the particular application method. After application, the solvent is removed by ambient drying or by forced drying in heated ovens or tunnels.

Solvent cements encompass a wide range of performance properties, from the simple natural rubber based cements which are widely used for low performance applications in homes and schools to the structural applications of contact adhesives based on polychloroprene and reactive phenolic resins.

### Latex Adhesives

A rubber latex is a two-phase system consisting of particles of rubber dispersed in water. Protective colloids and other stabilizing agents will be present in a latex to keep the rubber well dispersed and to prevent agglomeration or coagulation of the rubber particles. Natural rubber is collected as a latex from certain species of tropical trees, in particular, *Hevea brasiliensis*. The rubber particles exist as globules of 1–3 microns diameter at a solids level of 35–40%.

A number of synthetic rubbers are produced by emulsion polymerization and are, therefore, available in latex form. Those of greatest commercial interest are SBR, acrylic, neoprene, and vinyl acetate–ethylene. Rubber latexes, particularly natural and SBR, have been used for many years in carpet and upholstery backsizings, bag, shoe, and bookbinding adhesives, tile mastics, tire cord dips, and wookworking adhesives.

Environmental concerns, which have resulted in restrictions on the use of organic solvents, have been the impetus for a strong interest in the use of rubber latexes in the formulation of pressure sensitive tapes and labels, can sealants, and contact adhesives. The availability of suitable rubber latexes and tackifying resin dispersions have made this change pos-

sible, and pressure sensitive adhesives based on natural rubber, SBR, and acrylic latexes have become a significant part of the adhesive industry. The production of tackifying resin dispersions will be discussed in more detail later in this chapter.

Latex adhesives offer several advantages over solvent systems. In addition to being more environmentally acceptable, latex systems offer minimum fire hazards, easy cleanup of equipment, and higher solids content. A rubber latex is considerably less viscous at much higher solids content than a corresponding solvent system.

Natural rubber latex at 40% solids is much lower in viscosity than a 15% solids solution of milled rubber in toluene. In addition, the natural rubber in latex form is of much higher molecular weight than the milled rubber. This higher molecular weight yields much higher shear resistance when formulated into pressure sensitive adhesives.

A key aspect of formulating latex adhesives with rubber and resins is the compatibility of the individual latexes. Dispersing agents may be cationic, nonionic, or anionic. Knowledge of the chemical nature of the systems is critical to preventing coagulation of the solids when blending a rubber and a resin latex.

While solvent cements may provide greater ultimate strength than latex systems, the latter types find wide use and are often necessary for certain bonding requirements. Solvent systems penetrate into a porous substrate, with the result that multiple applications are often necessary to put enough adhesive on the surface to form a satisfactory bond. Since latex systems exhibit better “hold-out” on porous surfaces, one coat of such an adhesive is often sufficient for good bonding.

### Mastics

Mastics constitute a special type of adhesive which may be either latex or solvent-based. The unique characteristic of mastics is their extremely high viscosity. Most mastics contain natural rubber, SBR, or a blend. Some asphalt or bitumen may be added to lower raw material cost. Tackifiers and fillers are widely used.

Mastics are used in large volume, chiefly in



industrial applications and in the construction industry, where low bond strengths are adequate. They are used to install vinyl, rubber, or wood floor tiles, ceiling and ceramic wall tiles, vinyl and linoleum sheets, indoor-outdoor carpeting, and in the automotive industry for fastening insulation, silencer, and lining pads.

A simple latex mastic for applying ceramic tiles and wood flooring can be made by adding a high solids solution ( $>80\%$  solids) of an appropriate tackifying resin to an SBR latex with sufficient agitation to disperse the resin in the latex. Fillers may also be used in such a formulation. Such a mastic would then be applied to the floor or wall by trowel. The tile to be bonded is applied immediately with pressure before a skin forms on the mastic.

### Pressure Sensitive Adhesives

Pressure sensitive adhesives constitute the fastest growing segment of the rubber-based adhesive industry. A variety of pressure sensitive tapes and labels are available, such as:

- Tapes:
  - Packaging.
  - Medical.
  - Masking.
  - Office/consumer.
- Labels:
  - Permanent.
  - Removable.
  - Low temperature/freezer grade.
  - Film and foil.

Pressure sensitive adhesives, unlike cements or hot melt packaging adhesives, are formulated to remain permanently tacky at the application use temperature. The challenge to formulate such products has been met by the development of specially designed tackifying resins and polymers. Such adhesives are characterized by rapid adhesion to the bonding surface. By the proper choice of polymer and resins, the adhesion characteristics can be varied to give permanent or removable adhesives as well as adhesives which show either adhesive or cohesive failure upon peeling. These formulating principles will be discussed in more detail in the section on tackifying resins.

The first commercial applications of pressure

sensitive tape were in surgical tape and in friction tape for electrical, plumbing, and similar fastening applications. These were typically cloth-backed tapes which did not necessarily strip cleanly from the contacted surface. Later developments yielded general purpose masking tapes for household use and high-temperature resistant masking tapes for automotive painting applications. Polypropylene film-backed packaging tapes constitute a significant portion of the pressure sensitive tape industry today.

Pressure sensitive tapes and labels are offered with a variety of backing materials such as crepe paper, aluminum foil, fabric, cellophane, kraft paper, cellulose acetate, polyester film, polyethylene, polypropylene, plasticized poly(vinyl chloride), woven glass fiber cloth, or other flexible materials. Pressure sensitive adhesives may be applied from solvent, latex, hot melt, or radiation cured 100% solids systems. A wide variety of coating methods are utilized such as roll coating, calendering, slot die, and transfer coating.

A key factor in the growth of pressure sensitive adhesives has been the development of elastomers specially designed for pressure sensitive applications. Natural rubber is an important elastomer in these applications, as are carboxylated SBR latexes and solvent and latex acrylic. The thermoplastic block copolymers based on styrene endblocks and a rubbery mid-block of isoprene, butadiene, or ethylene-butylene, and the styrene-butadiene multiblock copolymers have become established as the elastomers of choice in some of the fastest growing segments of the pressure sensitive adhesive industry. These highly stable and versatile materials offer a combination of properties which permit the formulation of high-performance adhesive systems. The unique molecular block structure of these copolymers offers special challenges to the adhesive formulator, and these will be discussed in more detail in the section on tackifying resins.

### Hot Melt Adhesives

The class of adhesives applied in hot melt form has become a significant part of the adhesive industry in recent years. The environmental

pressures on solvent based adhesives which has given impetus to latex adhesives have also given increased impetus to developing suitable hot melt systems. A key reason for the growth of hot melt adhesives has been the development of more thermally and oxidatively stable modifying resins and elastomers.

These thermoplastic hot melt adhesives are composed of 100% solids nonvolatile materials, i.e., containing no water, solvents, etc. They are solid at room temperature, but melt and flow readily at application temperature, 275–350°F. After application, bonding and cooling, hot melt adhesives return to a solid state and develop their ultimate strength.

The early hot melt adhesives were not strictly definable as rubber-based adhesives. Most “rubber” polymers such as natural rubber and random SBR are of such molecular weight and structure that they do not melt readily to a workable coating consistency at a temperature below which thermal degradation and decomposition take place. Certain synthetic polymers, however, lend themselves to the formulation of a wide range of hot melt adhesive compositions. Polyamide and polyester resins, ethylene-vinyl acetate (EVA) copolymers, ethylene-ethyl acrylate (EEA) copolymers, low molecular weight polyethylene and amorphous polypropylene, and certain vinyl ethers have found application in hot melt adhesives. These adhesives have found wide use in packaging, industrial, and construction applications.

The commercialization of the styrenic tri-block copolymers in 1965 and the introduction of the styrene butadiene multiblock copolymers in the early 1980s have caused an increased interest in the application of hot melt adhesives. Not only have these materials greatly expanded the applications of hot melts into product assembly such as disposable diapers and other sanitary products, but the ability to formulate hot melt pressure sensitive adhesives from these copolymers has been a boon to the pressure sensitive adhesive industry. Hot melt pressure sensitive adhesives are ideally suited where fast production speeds, relatively low raw material cost, and the elimination of the need to remove or recover solvent are essential to the favorable economics of the manufacturing process.

## FUNCTION OF RESINS IN ELASTOMER-BASED ADHESIVES

### Resin Types

In the formulation of early elastomer-based adhesives, it was soon learned that a simple system consisting of natural rubber alone gave only marginal performance as a finished adhesive. Most commercially available synthetic elastomers have little tack, either to themselves or to other surfaces. Modifiers were found to contribute improvement in the adhesive performance characteristics.

Tackifying and modifying resins are represented by a variety of products of many different chemical types and physical properties. To a new adhesive formulator, the array of resins offered must seem bewildering and the choice of an appropriate resin must seem to be nothing more than mix and test. There is, however, a body of knowledge concerning elastomers and resins which allows for a systematic approach to the selection of the best modifying resin for a particular system. This systematic approach will be discussed in more detail shortly.

The first point of confusion concerns the terminology of tackifying vs. modifying resins. Strictly speaking, all resins added to an adhesive formulation modify the properties of that system and thus would be considered modifying resins. The majority of resins are added to an elastomer to generate increased tack or adhesion properties and are, thus, correctly called tackifying resins. Resins used in EVA, polyethylene, or other non-pressure sensitive hot melt adhesives are incorporated primarily to modify the viscosity and control open time. Thus, they are more correctly called modifying resins. With the development of block copolymer-based pressure sensitive adhesives, another class of resin, the endblock reinforcing resin, has come into widespread use. These resins associate only with the styreneic blocks of the copolymers and increase the shear resistance of the adhesive formulation.

Modifying resins have the following characteristics:

1. Low molecular weight, thermoplastic polymers ( $M_w$  200–2000);
2. Viscous liquids to hard, brittle glasses at room temperature;

3. Obtained from the derivatization of rosin or by the polymerization of petroleum distillates, turpentine fractions, coal tar, and pure monomers;
4. Range from water-clear to dark brown or black in color; and
5. Are soluble in aliphatic and aromatic hydrocarbons as well as in many other common organic liquids.

The general classes of resins, based on their chemical nature, are:

1. Rosin, modified rosin, and rosin derivatives;
2. Hydrocarbon resins; and
3. Terpene resins.

Rosin resins are produced from the three types of rosin—gum, tall oil, and wood. Fig. 1 shows the sources and processing steps used to obtain rosin from pinewood.

Although unmodified rosin has some application in low quality mastics and construction adhesives, rosin is typically modified to enhance its oxidative and thermal stability and to obtain a range of physical properties such as softening point and melt viscosity. Rosin is a complex mixture of tricyclic unsaturated resin acids with some nonacidic components. At least

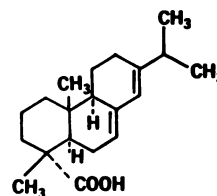


Fig. 2. Abietic acid.

twelve resin acids have been identified. Abietic acid, Fig. 2, is a common resin acid.

The derivatization of rosin focuses on the carboxyl group and the double bonds. Double bond reactions such as isomerization, hydrogenation, dehydrogenation, polymerization, and Diels-Alder adduction are typically carried out. Reactions of the carboxyl group include salt formation, esterification, hydrogenolysis, ammonolysis, and decarboxylation. Fig. 3 is a schematic of rosin derivatization carried out by one manufacturer, Hercules Inc.

Hydrocarbon resins are typically classified by the chemical nature of the feedstreams used, i.e., aliphatic, aromatic, cycloaliphatic, or mixed aliphatic-aromatic feedstreams. The main classes of resins commercially available are:

1. Aliphatic resins (C-5);
2. Aromatic resins (C-9);

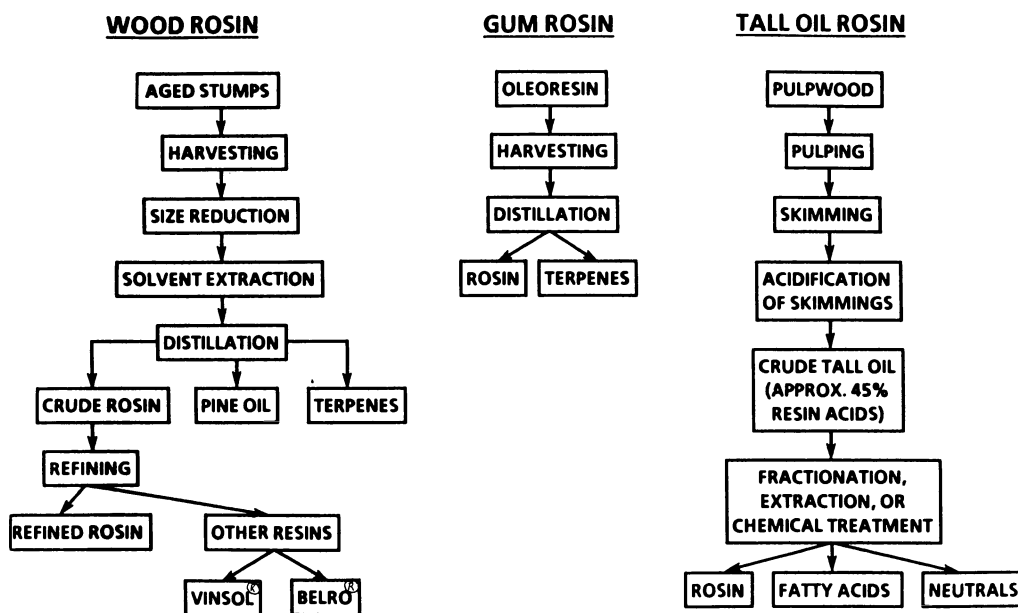


Fig. 1. Sources of rosin from pine wood.

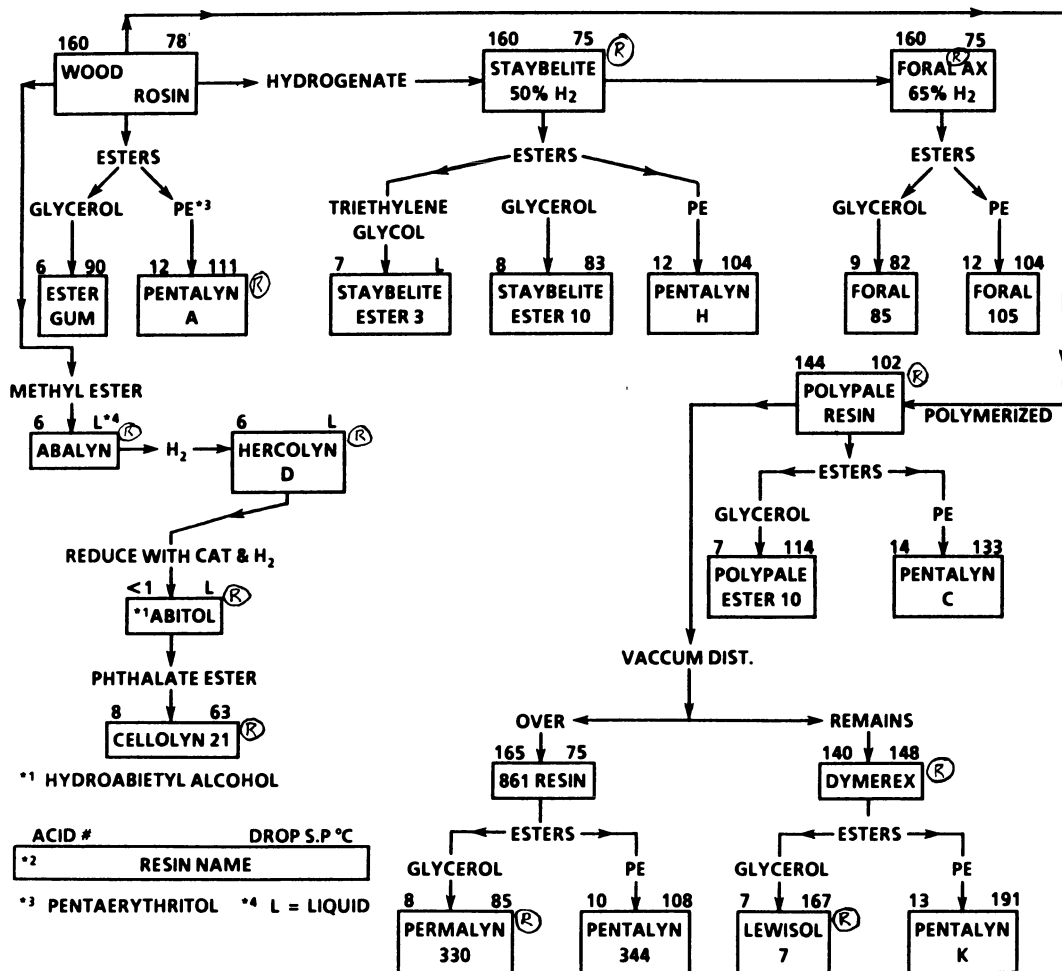


Fig. 3. Hercules, Inc., rosin derivatization.

3. Aromatic/aliphatic resins (C-5/C-9);
4. Pure monomer resins based on styrene, alphamethylstyrene (AMS), and vinyltoluene; and
5. Hydrogenated resins.

Polyterpene resins, aromatic-modified terpene resins, and phenolic-modified terpenes are produced from  $\alpha$ -pinene,  $\beta$ -pinene, *d*-limonene, and dipentene. Examples of the various resins listed by chemical type, trade name, physical properties, and manufacturer are found in Table 1.

### Tack

Before discussing the function and selection of resins for adhesives, some discussion of tack

and adhesion is necessary. To produce a suitable adhesive, three key criteria are required:

1. Tack or wetting properties;
2. Adhesive strength; and
3. Cohesive strength.

Tack is a term that is difficult to define in specific terms. Tack frequently represents a combination of many physical properties. Measurement of tack by application of finger pressure, a common technique, is obviously not quantitative. In adhesives technology, tack may be defined as the property of a material which enables it to form a bond of measurable strength immediately upon contact with another surface, usually with low applied pressure. Tack is thus "instantaneous" adhesion and differs

**Table 1. Modifying Resins—Types and Properties.**

Resin Type	Trade Name	Acid No.	Softening Point, °C		Manufacturer
			Drop <sup>a</sup>	R&B <sup>b</sup>	
Rosins:					
Gum rosin		165		78	China, Brazil
Tall oil rosin		163		80	5, 6
Wood rosin	Pexite®	160	80	73	1
Modified Rosins:					
Polymerized rosin	Poly-pale resin	144	102	95	1
Hydrogenated rosin	Staybelite	160	76	68	1
Disproportionated rosin	Dymerex resin	140	148		1
Rosin Esters:					
Pentaerythritol-wood rosin	Pentalyn A	12	111		1
Glycerine-hydrogenated wood rosin	Staybelite Ester 10	8	83		1
Pentaerythritol-hydrogenated wood rosin	Pentalyn H	12	104		1
Glycerine-highly hydrogenated wood rosin	Foral 85	9	82		1
Pentaerythritol-stabilized rosin	Pentalyn 344	10	104		1
Hydrocarbon Resins:					
Aliphatic petroleum	Piccotac® series	0		70-115	1
	Escorez® series	0		90-115	2
	Wingtack® series	0		86-115	3
Aromatic petroleum	Piccovar® series	0		10-60	1
	Picco® 5000 series	0		70-140	1
	Nevchem® series	0		70-150	4
Dicyclopentadiene	Piccodiene® 2215	0		115	1
Heat reactive	Neville® LX series	0		90-155	4
Aromatic modified aliphatic	Hercotac® 1149	0		96	1
	Super Sta-Tac®	0		80-100	7
Polymerized Terpenes:					
Alpha-pinene	Piccolyte® A series	0		115-135	1
d-Limonene	Piccolyte C series	0		10-135	1
Beta-pinene	Piccolyte S series	0		10-135	1
Aromatic modified	Zonatac® 105	0		105	5
Terpene phenolic	Nirez® 2000 series	0		122-148	7
Polyterpene	Nirez 1000 series	0		10-135	7
Pure Monomer Resins:					
Styrene/AMS	Kristalex® series	0		25-140	1
AMS/vinyl toluene	Piccotex® series	0		75-120	1
Styrene	Piccolastic® series	0		5-75	1
Hydrogenated Hydrocarbon:					
Cycloaliphatic	Regalrez® series	0		18-138	1
	Escorez 5000 series	0		80-120	2
	Super Nirez series	0		100-120	7
	Regalite® series	0		70-120	1
Reinforcing Resins					
	Endex® series	0		155-160	1
	Kristalex 5140	0		140	1
	Cumar® Lx-509	0		155	4

<sup>a</sup>Hercules drop softening point<sup>b</sup>ASTM Method E28-67 Ring & Ball method**Manufacturers:**

1. Hercules Inc.
2. Exxon Chemical Co.

3. Goodyear Chemicals.
4. Neville Chemical Co.

5. Arizona Chemical Co.
6. Union Camp Corp.

7. Reichhold Chemicals, Inc.

from final strength. The time required for development of strength by means of tack is very short compared to the time allowed for development of maximum strength. The measurement of tack of a pressure sensitive tape or label when the adhesive is applied to a surface without applied pressure and then immediately removed is known as *quick stick*.

Tack is a function of the rheological properties of the adhesive as well as the surface energy characteristics of the adhesive and the bonded surface. Resins modify both the rheological properties and surface energy of the adhesive formulation to give the proper flow and wetting characteristics. Tack is sensitive to variations in temperature, pressure, rate of application and removal of pressure, and contact time.

Adhesive strength refers to the strength of the bond produced by contact of an adhesive to a surface. Again, this ultimate strength will depend on temperature, pressure of application, and time of contact. Adhesion of pressure sensitive adhesives is usually measure by a peel test.

Cohesive strength refers to the internal strength of an adhesive or the ability of the adhesive to resist splitting. The clean peel of an adhesive from a surface requires that the cohesive strength of the adhesive be greater than the adhesive strength to the bonded surface. Unlike tack and adhesion, which are dependent on the surface being bonded, cohesive strength is not influenced by the substrate.

### Tackifier Function

Tackifying resins enhance the adhesion of non-polar elastomers by improving wettability, increasing polarity, and altering the viscoelastic properties of the adhesive mass. The understanding of how resins modify the viscoelastic properties of elastomers has developed significantly since the later 1960s. In 1966, C. Dahlquist<sup>2</sup> defined the performance of pressure sensitive adhesives on the basis of creep compliance. Sherriff, Aubrey, and co-workers<sup>3</sup> later demonstrated the effect of adding low molecular weight resins to natural rubber and exam-

ined the relationship between viscoelasticity and peel adhesion of rubber-resin blends.

More recently, Class and Chu<sup>4</sup> extended the use of dynamic mechanical measurements to a systematic study of resin-elastomer blends which revealed the relationship between the structure, concentration and molecular weight of resins and their effect on the viscoelastic properties of elastomers. Dynamic mechanical data typical of that obtained from an elastomer or elastomer-resin blend is shown in Fig. 4.  $G'$  is the elastic or storage modulus,  $G''$  is the viscous or loss modulus, and the ratio of  $G''/G'$  gives the  $\tan \delta$  curve. The temperature at which the  $\tan \delta$  curve shows a maximum corresponds to a dynamic glass transition temperature. Class and Chu showed that with these types of measurements, the effect of modifying resins on the viscoelastic properties of elastomers can be readily determined. Resins which are compatible with an elastomer will cause a decrease in the elastic modulus  $G'$  at room temperature and an increase in the  $\tan \delta$  peak or glass transition temperature. Resins which are incompatible with an elastomer will cause an increase in the elastic modulus  $G'$  at room temperature and will show two distinct maxima in the  $\tan \delta$  curve.

Chu has also characterized numerous commercial pressure sensitive adhesives and shown that elastic modulus and glass transition temperature are key viscoelastic properties in characterizing pressure sensitive adhesive performance. An excellent review outlining the characterization of pressure sensitive adhesive by dynamic mechanical measurements and discussing how these data can aid in the formulating of adhesives has been recently published by Chu.<sup>5</sup>

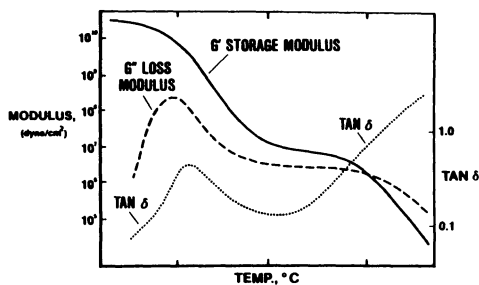


Fig. 4. Viscoelastic properties of polymers.

### Tackifier Selection

The major factors which determine the utility of a resin as a tackifier are:

1. Chemical structure;
2. Molecular weight; and
3. Molecular weight distribution.

Other factors of importance are:

1. Softening point;
2. Initial color;
3. Color stability when heated; and
4. Oxidative and UV stability.

The modification of an elastomer by a low molecular weight resin is determined by the compatibility (or solubility) of the resin in the elastomer. Compatibility is necessary for generating tack, but compatibility does not insure that the desired adhesive properties will be obtained. Rheology studies have shown that adhesive performance is related to the elastic modulus at application temperature and to the glass transition temperature of the resin-elastomer blend. A tackifying resin has a glass transition temperature higher than that of an elastomer. The glass transition temperature of

the resin-elastomer blend will thus increase as the level of resin is increased. The decrease in the elastic modulus will be determined by the compatibility of the resin with the elastomer. Thus, a formulator may be working with a compatible resin-elastomer blends but only certain combinations will allow him to obtain the desired level of elastic modulus and glass transition temperature.

An adhesive formulator has limitations on the amount of resin which can be incorporated into an elastomer in an attempt to obtain the desired combination of rheological properties. All resin-elastomer blends show a variation in adhesive properties vs. the concentration of resin. Fig. 5 shows probe tack as a function of resin concentration for a natural rubber-resin ester blend. This type of resin response curve is typical of all adhesive systems. In Fig. 5, little enhancement of tack is seen up to 40% resin concentration. Between 40 and 65% resin, there is a rapid increase in tack, followed by an equally rapid drop off in tack above 65% resin. Above, 65%, the system becomes overloaded in resin, incompatibility develops, and tack drops. The maximum in a resin response curve will be determined by the general compatibility

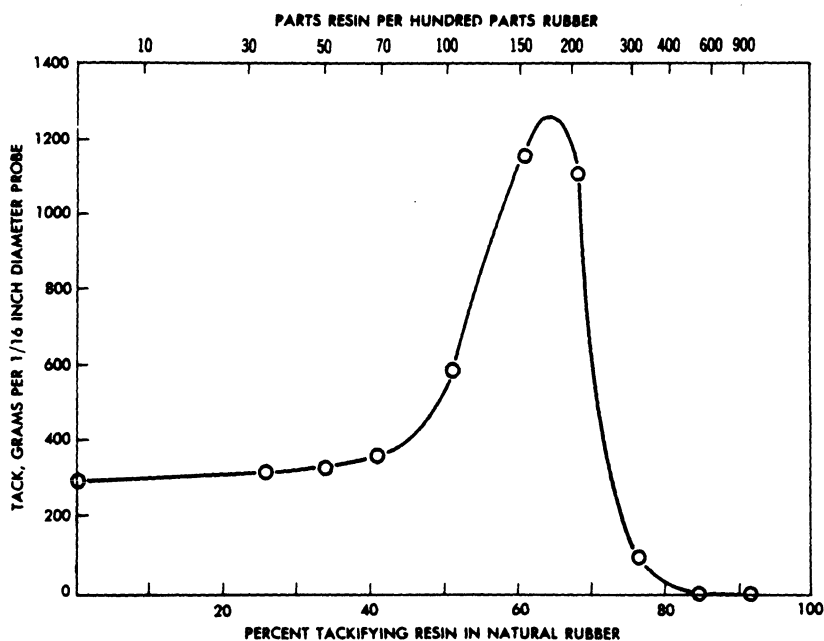


Fig. 5. Probe tack vs. resin concentration for natural rubber-resin ester blend.

of the resin with the elastomer. Typically, the lower softening point versions of chemically similar resins will develop maxima at higher resin loadings than the higher softening point resins.

A simple test of compatibility is the clarity of a resin-elastomer blend. A 1 : 1 blend can be prepared in solution and cast onto a glass plate. The solvent is allowed to evaporate and the cast film observed for clarity. A clear film indicates good compatibility while a cloudy or opaque film indicates some degree of incompatibility.

A more quantitative indication of compatibility can be obtained with solvent or hot melt cloud point tests. The solvent cloud point tests are based on the idea that resins will be compatible with elastomers of similar chemical nature. Thus aliphatic resins will be effective tackifiers for aliphatic elastomers such as natural rubber, while aromatic resins are needed for aromatic elastomers such as SBR. Some resins, e.g., rosin esters, will be compatible with many different types of elastomers. Solvent cloud point tests are carried out in three solvent systems which represent aliphatic, aromatic, and polar systems. The solvent blends used by Hercules are:

1. Odorless mineral spirits (OMS), an aliphatic solvent;
2. Diacetone alcohol/xylene (DACP), a polar blend; and
3. Methylcyclohexane/aniline (MMAP), an aromatic blend.

The resin is dissolved in the test solvent either at room temperature or at elevated temperature. The solution is then cooled and the temperatures at which an initial and full cloud appears are recorded. Low cloud points indicate good solubility in that solvent type and predict good solubility of that resin in elastomers of the same chemical nature. As a rule of thumb, cloud points greater than 70°C indicate poor compatibility while cloud points less than 0°C indicate excellent compatibility. Table 2 shows cloud points for four types of resins—rosin esters (Staybelite 10 Ester and Foral 85, 105), pure monomer aromatics (Piccotex), polyterpene resin (Piccolyte), and C-5 aliphatic resins (Piccopale, Piccotac). The low cloud points of the rosin esters in all blends predicts that rosin es-

**Table 2. Resin Cloud Points.**

<i>Resin</i>	<i>DACP, °C</i> ( <i>Polar solvent</i> )	<i>MMAP, °C</i> ( <i>aromatic</i> )	<i>OMSCP, °C</i> ( <i>aliphatic solvent</i> )
Staybelite 10	<0	<0	< -10
ester	<0	2	< -10
Foral 85	<0	15	< -10
Foral 105			
Piccotex 120	<0	10	60
Piccotex 75	<0	0	-22
Piccolyte S-115	56	87	< -10
Piccolyte S-135	61	95	< -10
Piccopale® 100	70	97	10
Piccotac B	55	90	< -10

ters would have wide compatibility with most elastomers—a fact that is well known. The other resins show more selectivity. The high cloud points in the polar and aromatic solvent blends in conjunction with a low OMS cloud point explains why C-5 aliphatic resins are compatible only with aliphatic elastomers such as natural rubber and the isoprene midblock of the styrene-isoprene-styrene block copolymer. Hot melt cloud point test can also be carried out with resin/polymer blends.

The choice of resin tackifier influences not only the initial adhesive performance, but also the retention of adhesive properties upon aging. Color retention and resistance to oxidation and UV degradation are key considerations in choosing a tackifying resin. Glycerine or pentaerythritol esters of unmodified wood rosin exhibit fair tack properties initially, but have poor aging characteristics primarily because of resin oxidation. Esters of rosins which have been stabilized by hydrogenation or polymerization, e.g., Foral 85 or Foral 105, possess the best combination of properties for adhesive use.

The stability of hydrocarbon resins varies greatly depending on chemical structure. Residual unsaturation in the resin molecule is the point for oxidative attack. Aliphatic C-5 resins and terpene resins can be protected with antioxidants to give good aging characteristics. Aromatic resins vary considerably in structure, but generally show good oxidative resistance. The most stable modifying resins available are those classified as hydrogenated resins. These resins are the result of hydrogenating aromatic,



aliphatic, or cycloaliphatic resins to remove as much unsaturation as possible. The water-clear initial color and color stability under oxidative, UV, and elevated temperature conditions make these the resins of choice for high-performance applications.

The development of the styrenic block copolymers has created special challenges for resin manufacturers. These block copolymers are of two basic types. The first are the *triblock copolymers*, consisting of an elastomeric midblock and thermoplastic polystyrene endblocks. These can be either the linear triblock copolymers, such as the Kraton polymers from Shell Chemical Company or the Europrene polymers from Enichem, or radial block copolymers, initially produced by Phillips Petroleum and now available from Petrofine SA under the tradename Finaprene. The linear triblock copolymers are the most widely used in the adhesive industry.

The second type of polymer is the *multiblock copolymer* based on styrene and butadiene, available from Firestone Synthetic Rubber and Latex Company under the tradename Stereon. This material has a much higher level of styrene than do the triblock copolymers (43% vs. 30% max.), but the formulation techniques used with this material would be similar to those used to compound a styrene-butadiene triblock copolymer.

Block copolymers, like most elastomers, require modifying resins to develop the desired adhesive properties. Tack is built into the formulation by the use of midblock associating resins, while enhanced thermal resistance and strength properties can be obtained by the use of endblock associating resins. The challenge to resins suppliers has been to design resins that will associate exclusively with the desired phase. Resins that associate with both phases are desired in some cases, and they can be effective tackifiers, but they typically cause a severe loss in the cohesive strength of the formulation. Table 3 lists modifying resins for block copolymers.

Table 4 shows the effect of molecular weight and molecular weight distribution on the tackifying effectiveness of three C-5 aliphatic resins. These three resins have softening points in the range of 92–100°C. Based on chemical

**Table 3. Modifying Resins for Block Copolymers.**

A. Midblock Tackifiers:
Rosin esters
Aliphatic C-5 hydrocarbon resins
Terpene resins
Aromatic-modified aliphatic resins
Hydrogenated resins
B. Endblock Compatible Resins:
Rosin esters
Aromatic resins
Low molecular weight resins
C. Endblock Reinforcing Resins:
High softening point aromatic resins

**Table 4. Adhesive Performance—Effect of Mw and MWD.**

SIS	100	100	100
Piccotac® 95	100		
Piccotac® B		100	
Piccopale® 100			100
Quick Stick, oz/in.	66	38	1
180° Peel, oz/in.	105	80	35
Shear resistance, (min)	10,000+	10,000+	—
SAFT, °C	105	105	—

structure, all three of these resins should be compatible with the isoprene midblock of a styrene-isoprene-styrene block copolymer. Piccopale 100, with the highest molecular weight and broadest molecular weight distribution, generates poor adhesive properties. Piccotac B, intermediate in molecular weight and molecular weight distribution, generates reasonable properties, while Piccotac 95, with the lowest molecular weight and narrowest molecular weight distribution, generates maximum adhesive properties. These data thus show that in a homologous series of resins, the lowest molecular weight resin with the narrowest molecular weight distribution generates optimum tack properties. There may be, however, other considerations such as optimizing shear resistance in a pressure sensitive adhesive that would cause a formulator to choose a resin that does not give optimum tack.

## LATEX-BASED PRESSURE SENSITIVE ADHESIVES

It has been previously mentioned that government restrictions on the use of organic solvents

enacted in the 1970s gave impetus to the development of latex-based pressure sensitive adhesives. Although a number of synthetic elastomer latexes were commercially available along with the natural rubber latex, most of these latexes were not ideally suited for pressure sensitive adhesive formulation. Latex manufacturers and resin suppliers thus began development programs which have resulted in SBR, acrylic, and vinyl acetate-ethylene latexes well suited for pressure sensitive adhesive applications and resin emulsions that are effective tackifiers for these elastomers.

Resin dispersions can be prepared in two general ways. In the direct method, a liquid material is added directly to an emulsifier solution and dispersed with good agitation. If the resin is solid at room temperature, it must be either dissolved in a organic solvent or melted and added molten to the aqueous phase. Any organic solvent is usually undesirable and must be removed after emulsification.

In the inversion method, a water in oil emulsion is first formed by slowly adding water to the resin phase in the presence of an emulsifier. As more water is added, an inversion point is reached at which water becomes the continuous phase and the dispersion becomes an oil in water emulsion. Fine particle sizes are developed by shearing the viscous mass at the inversion point. After inversion, water is added to reach the desired solids level which is typically 55–60% solids.<sup>6</sup>

The key emulsion properties that a resin supplier attempts to control are:

1. Total solids;
2. *pH*;
3. Particle size;
4. Viscosity;
5. Mechanical stability;
6. Surface tension;
7. Freeze-thaw stability; and
8. Ion tolerance.

A number of factors must be considered in blending elastomer latexes and resin dispersions. A formulator must determine that the emulsifier systems are compatible. Many resin dispersions are prepared with anionic emulsifiers based on rosin acids. The *pH* of these

emulsions can be as high as 10–12. If such a resin emulsion is blended with a low *pH* elastomer latex, latex shock will often result and the elastomer and resin will coagulate. Latex shock can be minimized by the use of additives to the resin emulsion, but even similarity of *pH* does not always insure latex compatibility.

Many anionic emulsifier systems are susceptible to coagulation by strong acids or multivalent cations. Again, additives can enhance the ion tolerance of resin emulsions, but careful testing is necessary.

Stability to shearing forces is critical to latex adhesives. Pumping and coating operations put high shear forces on the latex which will result in coagulation and grit formation if sufficient mechanical stability is not present.

Once the proper compatibilities and stabilities are obtained, the elastomer-resin blend can be prepared. At this point, another difference between solvent or hot melt and latex adhesives arises. In solvent or hot melt systems, at the time of application, the resin and elastomer are intimately mixed. Removal of solvent or cooling results in the desired adhesive properties. In a latex system, the degree of mixing of the components is not as extensive. Merely removing the water at room temperature usually does not result in the desired level of tack. Some heating of the system is required to mix the components on a molecular scale and achieve the desired adhesive properties. The softening point of the tackifier resin is usually the determining factor in how much heating must be applied. Low softening point resins will diffuse more readily into the elastomer and require less heating. Fig. 6 is a schematic of this process.

Even when the adhesive properties are obtained, emulsifier aging characteristics remain a concern. Migration of the emulsifier to the surface of the adhesive can cause loss of adhesion. In addition, the moisture resistance of the dried film must be determined. Some emulsifiers show a strong tendency to absorb moisture from the atmosphere and to re-emulsify the top layer of adhesive, resulting in the loss of adhesion.

Resin manufacturers, elastomer producers, and adhesive formulators have combined their knowledge to control the many factors in latex adhesive formulation. The result is a growing

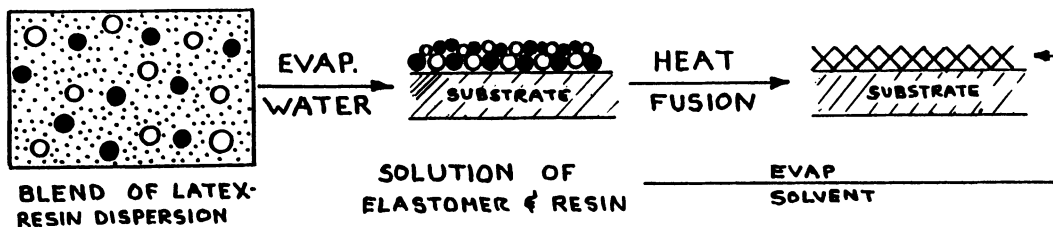


Fig. 6.

application for latex adhesives, particularly in pressure sensitive tapes and labels.

### PRESSURE SENSITIVE ADHESIVE TEST METHODS

The Pressure Sensitive Tape Council<sup>6</sup> has developed a series of test procedures for the determination of tack, adhesion, and shear properties of pressure sensitive adhesives. The most commonly used tests are:

1. 90° quick stick;
2. 180° peel adhesion;
3. Rolling ball tack; and
4. Shear adhesion—room temperature and elevated temperature.

Quick stick is a measure of how readily a pressure sensitive adhesive adheres to a test surface with no applied pressure other than the weight of the adhesive backing. The test strip is peeled immediately after application.

Peel adhesion is the force required to remove a pressure sensitive tape or label from a test surface at a specified angle and rate of peel. This gives a measure of the ultimate strength obtained by the adhesive and the dwell time before peeling must be specified. In this test, the adhesive tape or label is applied to the test surface with a specified force.

Rolling ball tack is a unique test method in which a small ball of specified weight and diameter is rolled down an incline plane onto an inverted test adhesive strip. The distance the ball rolls before stopping is an measure of the tack properties of the adhesive.

Shear adhesion is a method of determining

the resistance to shear of a tape under constant load. It is the force required to pull a pressure sensitive tape from a standard test panel in a direction parallel to that surface. It is usually measured in terms of the time required for the tape to slip a certain distance. This test measures the cohesive strength of the adhesive bond.

Probe tack is a test in which a 0.5 cm diameter probe is contacted with an adhesive film at a specified application pressure and dwell time. The force required to remove the probe from the adhesive is a measure of tack.<sup>6</sup>

### ACKNOWLEDGMENT

The authors wish to acknowledge the contributions of their many Hercules colleagues who over the years have contributed to an understanding of resin chemistry and adhesives applications. The information in this chapter is compiled from their achievements.

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# Section C

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## Adherends and Bonding Technology

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# Bonding Plastics

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Modern products exploit many of the inherent design and manufacturing advantages of plastics. Although designing with molded plastic often allows a reduction in the number of parts needed, usually some assembly operations remain. Sometimes the product is too complex to mold in one piece, or it may require properties available only in metal, ceramic, elastomers, or other materials.

Selection of an assembly method is a critical step in the overall design process. It should be analyzed at the same time as other factors so that all elements contribute effectively to the product. Failure to do so raises the risk of discovering errors after the material has been selected and the mold fabricated. It is not safe to assume that a suitable bonding process exists for every combination of design, materials, and product operating environment.

## **BONDING DESIGN ADVANTAGES**

### **Material Versatility**

Bonding allows selection of nearly any plastic used by itself or in combination with elastomers, metals, glass, ceramics, wood or other plastics. No other assembly method is this versatile.

### **Even Stress Distribution**

The ability to spread load evenly over the joint area is especially important in plastic assembly.

Mechanical fasteners concentrate the stresses into a few areas in the joint.

While a rigid metal component may accommodate these stresses easily, a more flexible plastic part of the same cross section may require extra stiffening in the form of ribs, inserts, or bosses. Much of the design simplicity of molded parts can be lost in making provision for mechanical assembly. By contrast, a bonded joint requires no extra design provision other than a check to ensure that enough joint area is available and that the adhesive meets service requirements.

### **Fluid Tight Joints**

If fluid-tight joints are required, this requirement can readily be achieved with a bonded design. Mechanical joints usually require an extra sealing component such as an O ring. Extra sealing devices can add to the size, cost and overall complexity of the design.

### **Simplified Molding**

The shape of a product may make it impossible to mold without complex tooling. In many cases it is possible to lower costs by using several simpler moldings and bonding them together.

## **SURFACE INTERACTIONS IN BONDING**

In the most fundamental sense, successful joining of plastics always involves significant in-

teractions between the surfaces being joined and the bonding agents used in the process. The interactions involved can be as simple as penetration of an adhesive into a porous surface, or more complicated, as in the wetting of polymer surfaces. Whatever the mechanism, there can be no joint without some form of interaction.

Plastics are distinguished from metals and other traditional materials in that there are a wider variety of potential interactions that can contribute to the joint strength. In analyzing the situation, the following classification of interactions has been used by D.W. Aubrey.<sup>1</sup>

### **Mechanical Interlocking**

Most materials have some surface roughness or porosity which will allow an adhesive to penetrate before hardening. If significant porosity is present, as in a polymer foam, mechanical interlock can be the most significant single interaction contributing to strength and durability.

Joints based on mechanical interlock have predictable strength and durability since these properties are related to the bulk properties of the substrate materials and the adhesive layer. If the substrate materials and the adhesive selected are suitable for the environment, no trouble is expected with joint durability.

Even if the surface is not porous, the microscopic roughness present on most surfaces adds a mechanical contribution to the strength of the joint and increases the total interfacial area available for other bonding.

### **Physical Adsorption/Wetting**

Provided a liquid adhesive wets the surface of the plastic, attractive forces occur between the liquid and the two solids. The magnitude of these forces is directly related to the surface tension of the liquid and inversely to the gap between the components.

For closely fitted components, significant strength is achieved even with nonhardening liquids. If an adhesive is used, the hardening process strengthens the joint by adding resistance to shear and cleavage forces.

As will be discussed later, plastic bonding is

complicated by the fact that wetting of the plastic surfaces does not occur as readily as metal surfaces. Special attention may be required in preparing the surfaces for joining.

### **Molecular Diffusion and Interpenetration**

In adhesive bonding of metals, ceramics and other inorganic materials, it is assumed that no mixing of the adhesive and the substrates occur and that the interface is a well defined boundary between the two materials.

In the case of polymer joining, the assumption of no physical mixing is not reasonable. Welding of plastics, using heat or solvents, is a clear example of interpenetration occurring at the joint surface.

Other examples are less obvious and may go unrecognized. For example, cyanoacrylate adhesive is a solvent for some polymer surfaces, and may actually dissolve and mix with some of the surface before it hardens. As a result, the bonds exhibit excellent durability toward moisture and other environmental stresses, seemingly in contradiction to the adhesive's poor reputation for service under these conditions. The interpenetration provides durability which is absent when the same adhesive is used on an inorganic substrate.

When hot melt adhesives are used on plastics, a certain amount of interpenetration may occur if the hot melt causes surface melting of the substrate. In effect, such a joint may assume some of the characteristics of a weld.

## **JOINING PROCESSES**

Metal joining operations, such as welding, brazing, or bonding, are easily understood as distinct processes. However, the technologies tend to become blurred in the field of plastic joining owing to the variety of bonding interactions that are possible. The person joining plastics with a fluid may not be aware of whether a weld or an adhesive bond is being created, although the difference may be critical to the success of the joint. In describing the processes, efforts will be made to discuss the significance of the interactions that are occurring as well as the actual process.

## Solvent Welding and Cementing

Many thermoplastics can be welded together using organic solvents or combinations of solvents. In solvent welding, the solvent penetrates between closely fitted parts, dissolves the surface, and causes them to fuse together. When the solvent dries, strong, durable bonds are formed based on the interpenetration of the polymer chains.

The process is simple and low in cost, but requires close fitting parts and the availability of suitable solvents. While different plastics can be joined if both are soluble, joints involving inorganic materials or thermoset plastics are impractical.

Solvent cements contain dissolved polymer and can be used if gaps are present. These materials create a welding action if the substrate polymer is soluble, and at the same time will leave a gap filling film between the components. If porous substrates are used, mechanical interlock can take place. If surfaces are not soluble or porous, joint strength can still be generated if the cement wets the surface. Cements are capable of joining more types of materials than solvents alone, and will tolerate larger bondline gaps.

Solvent based joints require a carefully controlled process to achieve good results. The time between application and assembly is critical. If the time is too short, excess solvent is trapped in the joint. If the wait is too long, the film may dry too much and there may be insufficient flow to properly join the surfaces.

A trend toward greater regulation in handling solvents and cements is restricting the choices available. Safety issues should be addressed early in the selection process.

## Heat Welding, Ultrasonic Welding, and Electromagnetic Welding

These techniques share the common feature of heating the polymer surfaces above the melting point, joining them, and allowing them to cool under pressure. Since significant mixing and interpenetration of the polymers occurs, durable joints are created which often approach the strength of the plastic itself.

The methods differ in the manner in which the heat is generated. Heat welding uses contact with hot gasses or hot plates, while ultrasonic welding generates heat by rubbing the surfaces together at ultrasonic frequencies. Electromagnetic bonding utilizes induction heating of a ferromagnetic powder formulated into an adhesive or previously applied to the surface of the components.

## Adhesive Bonding

Adhesive bonding is the most versatile of these joining processes, since all classes of plastics and other materials can be joined. Adhesive bonding of plastic involves several of the joining interactions previously described, depending upon the characteristics of the adhesive and the substrates being joined.

1. In all cases mechanical interlock is present, since almost all surfaces have some degree of surface roughness or porosity. However, the degree of mechanical interlock can be extremely low in the case of plastic parts produced from highly polished molds.
2. The degree of physical absorption depends on whether or not the adhesive wets the surface. If good wetting occurs, this process can lend substantial strength to the joint. Without good wetting, it is difficult to achieve practical adhesive bond strengths.
3. It is sometimes easy to overlook the fact that molecular diffusion and interpenetration can occur during the formation of "adhesive bonds." Adhesives, by themselves or in combination with carrier solvents, can have a solvating effect on the surface of plastic parts. This in turn allows interpenetration of polymer molecules and may lead to bonds of exceptional durability.

## BONDING TECHNOLOGY

### Surface Wetting Criteria

As a first approximation, wetting of a surface occurs when the surface tension of the liquid adhesive is lower than the critical wetting ten-

sion of the solid surface. (See also Chapters 3 and 4.) If this condition is not met, the liquid does not spread and forms a round droplet on the surface—as when water beads up on a freshly waxed automobile.

In metal bonding the issue of wetting is easily settled. Clean metal surfaces have extremely high critical wetting tensions, in the order of several hundred dynes/cm. As a consequence, adhesives with a typical surface tension of 35 dynes/cm have little trouble wetting metal surfaces. If wetting problems occur, it is almost always the result of contamination on the substrate surface, a condition that can be quickly checked with the *water break test*. If water with a surface tension of 73 dynes/cm wets the surface, it is a safe assumption that no problem will be encountered with lower surface tension adhesives.

Unfortunately, wetting problems on plastics are not as easily resolved. Since adhesives and plastics are both polymers, they may have similar surface tensions and critical wetting tensions. Under the most favorable of conditions, adhesives will still wet the surface. However, plastics such as polytetrafluoroethylene, polyethylene, or polypropylene have such low critical wetting tension that bonding is not practical without surface treatments designed to raise its value.

### Surface Preparation

Conditions may require the use of surface preparation on plastics. Previously mentioned were cases in which the surface is too smooth for mechanical interlock or has too low a critical surface tension for wetting. In addition, other conditions may be critical. This includes the presence of mold releases, plasticizers, or other contaminants on the surface of the part. Methods of surface preparation are discussed below.

**Cleaning and Abrading.** One of the simplest methods of surface treatment is cleaning and abrading. The most common procedure is a solvent wipe, followed by abrasion and a final solvent wipe.

Grit blasting is often the most effective abrasion method. Aluminum oxide cloth is also effective. Commercial sandpaper should be

avoided, since it often contains lubricants to assist in finishing wood. Wipers used in the process should be free of sizing agents or other soluble contaminants.<sup>2</sup>

While cleaning and abrasion cannot always make large differences in bonding characteristics, using this procedure first insures that problems are not caused by surface contamination. Another potential benefit is that removal of the surface layer may expose polymer with better wetting and bonding characteristics.

**Flame Treatment** Flame treatment can be used as an effective means of changing the surface characteristics of plastics. Flame treating is accomplished by passing the surface of the plastic through the oxidizing portion of a natural gas flame. The surface is rapidly melted and quenched by the process and some oxidation of the surface may occur at the same time. Exposure time to the flame is a few seconds. While specially designed gas burners are available for this process, preliminary laboratory trails can be conducted using the outer (oxidizing) portion of an ordinary gas burner.

Flame treating is widely used for polyethylene and polypropylene, but also has been effective with thermoplastic polyester, polyacetal, and polyphenylene sulfide.

**Chemical Surface Treatments.** Chemical surface treatments are often used to improve plastic bonding. The most common involve strong oxidizing agents such as chromic acid to etch the surface. Polytetrafluoroethylene (PTFE) and other fluoropolymers are treated with etching solutions based on dispersions of metallic sodium in organic solvents. Surfaces treated in this way undergo dramatic improvement in wetting characteristics and can be readily bonded using a wide range of adhesives. In some cases it is possible to purchase PTFE treated in this fashion.

**Plasma Treatment.** Plasma surface treatment is a relatively new technology which is proving useful for improving wetting. In this process, parts are exposed to ionized gases generated by radio frequency energy in a sealed chamber under extremely low pressures. By se-



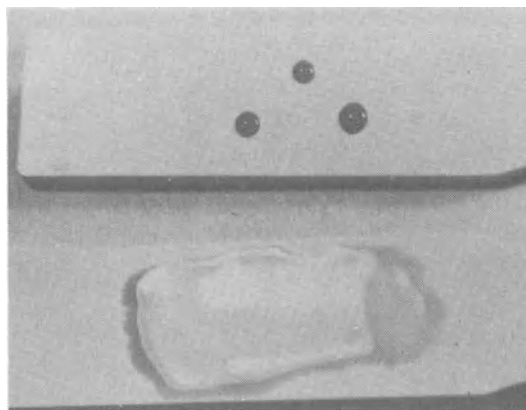


Fig. 1. Liquid beads on surface of polypropylene prior to plasma treatment (top). After treatment, liquid spreads (below). Surface tension of liquid is 35 dynes/centimeter.

lecting appropriate gases and exposure conditions it is possible to clean, etch, or chemically activate the surface. Significant differences in surface wetting can result (see Fig. 1). Bond strength is often increased by a factor of two to three. Because a closed chamber must be evacuated to employ plasma treatment, the process lends itself to large numbers of small, high-value parts. For larger parts it can be harder to justify economically, since fewer parts can be treated in one cycle.<sup>3</sup>

Landrock has compiled a comprehensive list of specific surface treatments for various types of plastics.<sup>4</sup>

### Solubility Parameter

In the second edition of this *Handbook*, Miron and Skeist stressed the importance of the solubility parameter in formulating adhesives for plastics. The concept of solubility parameter has been discussed in Chapter 1. Table 1 gives the solubility parameter for many plastics. Table 2 gives the solubility parameters of many solvents for plastics, along with their fractional polarities.

In comparing the data, Miron and Skeist found confirmation of many known facts about the solubility of plastics. "Polystyrene (8.6–9.1) is soluble in toluene (8.9), but not in hexane (7.3) or acetone (10.0). Tetrahydrofuran (9.9) and cyclohexanone (9.9), or mixtures of the two, are preferred solvents in dope cements

Table 1. Solubility Parameters of Plastics.

	$\delta$ , hildebrands
Polytetrafluoroethylene	6.2
Polychlorotrifluoroethylene	7.2
Polydimethyl siloxane	7.3–7.6
Ethylene-propylene rubber	7.9
Polyethylene	7.9–8.1
Polystyrene	8.6–9.1
Poly(methyl methacrylate)	9.3
Poly(vinyl chloride)	9.5–9.7
Amino resins	9.6–10.1
Epoxy	9.7–10.9
Polyurethane	10.0
Ethyl cellulose	10.3
Poly(vinylchloride-acetate)	10.4
Poly(ethylene terephthalate)	10.7
Cellulose acetate (secondary)	10.4–11.3
Cellulose nitrate	9.7–11.5
Phenol-formaldehyde	11.5
Poly(vinylidene chloride)	12.2
Nylon 6,6	13.6

Table 2. Solubility Parameter of Solvents.

	Solvent Parameter ( $\delta$ , hildebrands)	Fractional Polarity ( $p$ )
<i>n</i> -Perfluorohexane	5.6	0
<i>n</i> -Hexane	7.3	0
Cyclohexane	8.2	0
Amyl acetate	8.45	0.067
1,1,1-Trichloroethane	8.3	0.069
Carbon tetrachloride	8.6	0
Toluene	8.9	0.0001
Ethyl acetate	9.1	0.182
Trichloroethylene	9.2	0.005
Methyl ethyl ketone	9.3	0.510
Chloroform	9.3	0.017
Methyl acetate	9.6	0.182
Cyclohexanone	9.9	0.380
Tetrahydrofuran	9.9	—
Dioxane	10.0	0.006
Acetone	10.0	0.695
Carbon disulfide	10.0	0
Nitrobenzene	10.0	0.625
Dimethyl formamide	12.1	0.772
Nitromethane	12.6	0.780
Ethanol	12.7	0.268
Dimethyl sulfoxide	13.4	0.813
Ethylene carbonate	14.5	0.924
Phenol	14.5	0.057
Methanol	14.5	0.388
Water	23.2	0.819

for bonding PVC pipe (9.5–9.7 for the unplasticized homopolymer). Cellulose acetate (10.4–11.3) is dissolved in blends of acetone (10.0) with a minor proportion of ethanol (12.7).” In general the closer the values, the higher the probability that the solvent will be a good welding agent for the plastic. Such a solvent may also be a good pretreatment for the plastic to allow more interpretation between the substrate and adhesive.

If the adhesive application method requires a solvent, the solubility parameter of the substrate is a significant criterion for solvent selection. In practical cases it is not uncommon to change the solvent blend to get a better “bite” into the surface. In more precise terms, the solubility parameter of the adhesive solution is being adjusted to achieve a higher degree of interaction between the adhesive and the substrate.

### Adhesive–Plastic Compatibility

When bonding metals and other inorganic materials the issue of adhesive-to-substrate compatibility seldom arises. Cases of damage to these materials are few and are typically the result of unusual circumstances. However, in bonding plastics, care must be taken to avoid crazing or stress cracking. This occurs when incompatible adhesives or solvents are applied to the surface of a stressed plastic part. Softening and weakening of the surface leads to the formation of cracks. Liquid adhesive may penetrate into the crack, causing further damage. Eventually, the crack may propagate through the entire part leading to failure (see Fig. 2).<sup>5,6</sup>

Conditions necessary for stress cracking include:

- Stresses in the part, either from an external source or as the result of “frozen-in” molding pressures.
- Presence of liquid adhesive, as cured adhesive is not known to cause cracking.
- Time for both stresses and adhesive to interact. The length of the time interval is typically minutes, but may be as long as ten days depending upon the severity of the conditions.

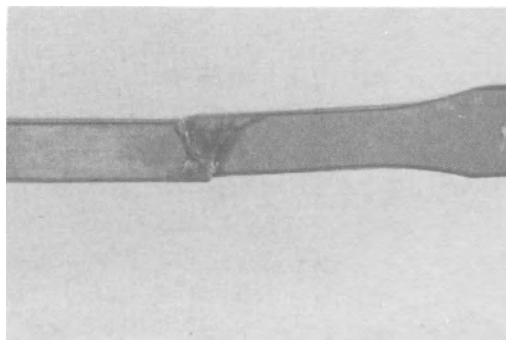


Fig. 2. Crack in polyetherimide tensile bar caused by exposure to incompatible solvent.

In most cases the possibility of stress cracking can be eliminated by following these guidelines:

- Work with parts that are in a low stress condition. If excessive stresses are molded in, they can be reduced by changing the molding conditions or by annealing the parts after molding.
- Use the minimum quantity of adhesive necessary and cure it as quickly as possible.
- Remove excess adhesive from parts as soon as possible.
- Use only cleaning solvents and primers which are compatible with the plastic.
- When in doubt, check with the suppliers of the plastic or the adhesive.

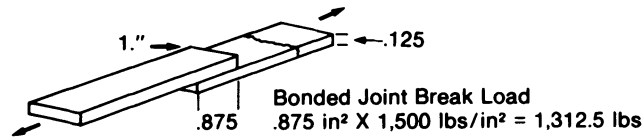
### ADHESIVE JOINT DESIGN FOR PLASTICS

Compared to metals and many other engineering materials, plastics have lower tensile strength, lower elastic modulus, and a higher coefficient of thermal expansion. These differences strongly influence the way joints are designed and adhesives are selected. In the paragraphs that follow the significance of these differences will be briefly analyzed.

The lower tensile strength of plastics makes it common to design lap joints that are stronger than the plastic itself. Consider the example of Fig. 3. The load capacity of the adhesive, acting over a shear area of 0.875 in.<sup>2</sup>, is greater than the tensile capacity of the plastic operating

**Plastic Break Load**

$$.125 \text{ in}^2 \times 7,000 \text{ lbs/in}^2 = 875 \text{ lbs}$$



- Plastic breaks at 875 lbs.
- Same overall assembly strength achieved with overlap of only .58 inch.

Fig. 3. Plastic fails before bond when large overlaps are used.

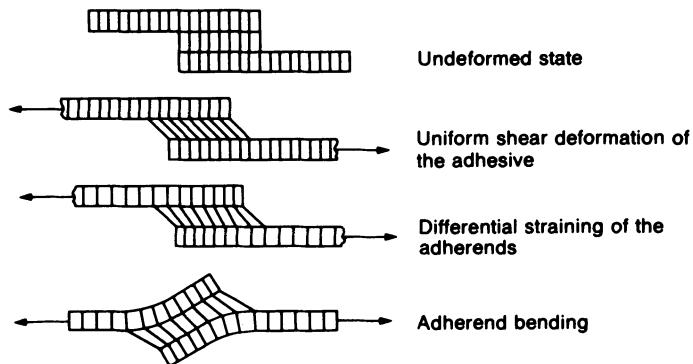


Fig. 4. Schematic drawings of bonded tensile lap-shear specimens, greatly exaggerated to illustrate effect.

**Table 3. Suitability of Joining Methods for Plastic Assembly.**

<i>Plastic</i>	<i>Adhesive</i>	<i>Solvent Welding</i>	<i>Heat Welding</i>	<i>Ultrasonic Welding</i>
ABS	Y	Y	Y	Y
Acetal	Y	N	Y	Y
Cellulosic	Y	Y	Y	Y
Nylon	Y	Y	Y	Y
Polycarbonate	Y	Y	Y	Y
Polyetherimide	Y	Y	Y	Y
Polyethylene	N	N	Y	Y
Polymethyl methacrylate	Y	Y	Y	Y
Polyphenylene oxide	Y	Y	Y	Y
Polyphenylene sulfide	Y	N	N	N
Polypropylene	N	N	Y	Y
Polystyrene	Y	Y	Y	Y
Polyurethane	Y	N	N	N
Polyvinyl chloride	Y	Y	Y	Y
Polytetrafluoroethylene	Y	N	N	N
Diallyl phthalate	Y	N	N	N
Epoxy	Y	N	N	N
Melamine	Y	N	N	N
Phenolic	Y	N	N	N
Thermoplastic polyester	Y	N	Y	Y
Thermoset polyester	Y	N	N	N
Urea	Y	N	N	N

on a cross-sectional area of only 0.125 in.<sup>2</sup>. As a result, the plastic breaks outside of the bonded joint area. If it is desired to increase the strength of the overall assembly, the best option is to increase the width of the bonded joint rather than the overlap. In this way, the load carrying

capacity of the plastic remains in balance with the bond strength. The use of thicker laps or a stronger plastic is also an option.

With an elastic modulus of approximately 300,000 psi, a typical unreinforced thermoplastic is over one hundred times more flexible

**Table 4. Selection Chart for Bonding Plastics to Themselves or Other Materials.**<sup>a, b</sup>

	1	2	3	4	5	6	10	11	12	13	14	21	22	23	24	25	26	27	41	42
<b>Thermoplastics</b>																				
ABS			Y	Y	Y	Y			Y	Y	Y		Y	Y	Y	Y		Y		
Acetal				Y		Y				Y	Y			Y	Y	Y		Y		
Cellulosic			Y	Y	Y			Y		Y						Y		Y		Y
Nylon			Y	Y							Y			Y	Y		Y	Y		
Polycarbonate			Y	Y	Y					Y	Y			Y	Y		Y	Y		
Polyetherimide					Y					Y	Y			Y	Y		Y	Y		
Polyethersulfone		Y	Y	Y	Y	Y		Y		Y	Y			Y	Y	Y	Y			Y
Polyethylene			Y		Y				Y	Y				Y	Y	Y	Y			Y
Polyethylene terephthalate				Y	Y			Y			Y			Y	Y	Y	Y			
Polymethyl methacrylate	Y	Y	Y	Y	Y	Y		Y		Y	Y				Y	Y	Y			Y
Polyphenylene oxide, modified			Y	Y	Y			Y		Y	Y			Y	Y	Y	Y	Y		Y
Polyphenylene sulfide				Y	Y	Y		Y	Y	Y	Y			Y	Y	Y	Y			Y
Polypropylene	Y	Y			Y				Y	Y				Y	Y	Y	Y			Y
Polystyrene		Y	Y		Y				Y	Y	Y			Y	Y	Y	Y			Y
Polyurethane				Y	Y						Y			Y			Y			
Polyvinyl chloride				Y	Y			Y		Y	Y			Y	Y		Y	Y		Y
Polytetrafluoroethylene					Y				Y				Y	Y						
<b>Thermosets</b>																				
Epoxy				Y	Y					Y			Y	Y	Y	Y	Y	Y		
Melamine			Y	Y	Y					Y	Y			Y	Y	Y	Y			Y
Phenolic	Y	Y	Y	Y	Y					Y	Y			Y	Y	Y	Y			Y
Polyester	Y	Y	Y	Y	Y					Y	Y			Y	Y	Y	Y	Y		Y
Urea	Y	Y	Y	Y	Y					Y	Y			Y	Y	Y	Y			Y
<b>Other Materials</b>																				
Ceramic	Y		Y	Y	Y	Y		Y		Y			Y	Y		Y	Y	Y		Y
Fabric			Y	Y	Y			Y					Y	Y	Y		Y			Y
Leather	Y		Y	Y	Y			Y		Y			Y	Y	Y	Y	Y			Y
Metal	Y	Y	Y	Y	Y			Y	Y		Y		Y	Y	Y	Y	Y	Y		Y
Paper	Y	Y		Y	Y			Y		Y			Y	Y		Y	Y			Y
Rubber	Y	Y	Y	Y	Y	Y		Y	Y	Y	Y			Y		Y	Y			Y
Wood	Y	Y	Y					Y		Y				Y	Y	Y	Y			Y

<sup>a</sup>Directions: (1) FOR PLASTICS TO THEMSELVES, CONSIDER ADHESIVES MARKED "Y". (2) FOR MIXED SUBSTRATE JOINTS, CONSIDER ADHESIVES MARKED "Y" ON BOTH SUBSTRATE LINES.

<sup>b</sup>Adhesive code numbers:

#### Elastomeric

1. Natural rubber
2. Reclaim
3. Neoprene
4. Nitrile
5. Urethane (also thermosetting)
6. Styrene-butadiene

#### Thermoplastic Resin

10. Acrylic
11. Cellulos nitrate
12. Polyamide
13. Hot-melt copolymer blends
14. Cyanoacrylate

#### Thermosetting Resin

21. Resorcinol phenolic
22. Epoxy
23. Reactive acrylic
24. Butyral phenolic
25. Polyester
26. Anaerobic
27. Silicone

#### Miscellaneous

41. Rubber latices
42. Resin emulsions

than a steel component of identical shape. In the design of bonded joints this means that elastic deformations, that could be safely ignored in metal joints, become critical. Instead of the uniform stress distribution normally assumed for lap joints, bending and differential straining of adherends can create extreme stress concentrations at the ends of the joint overlap (see Fig. 4).

These excess stress concentrations in lap joints can be effectively reduced by using more flexible adhesives, thicker or more rigid substrates, shorter overlaps, or thicker bond lines.<sup>7</sup>

When materials with different coefficients of thermal expansion are joined, shear stresses result when the assembly is heated or cooled. In the case of inorganic materials, problems have been noted in assemblies involving steel to aluminum or aluminum to glass even though the difference in expansion rates of these materials is relatively small.

In the case of plastics, the problem is aggravated by the fact that the potential differences in expansion rate can be up to an order of magnitude higher. This can best be prevented in the design stage by careful selection of materials. In cases where a mismatch is unavoidable, use of more flexible adhesives or thicker bondlines is helpful. Schneberger has suggested the use of flexible primers to help absorb some of the differential strain.<sup>8</sup> In extreme cases a rubber buffer can be bonded between the substrates to absorb the strain.

## SELECTION OF A BONDING METHOD

Bonding process selection can best be understood if it is thought of as an assembly method rather than a complex chemical technology. Bonding processes are functionally equivalent to other assembly methods such as screws or staples, but differ in that the chemical technology is less visible and understandable to the average user. The mechanical ingenuity behind a special mechanical fastener is easy to see, while the chemical ingenuity of a high technology adhesive may be lost in the complex jargon of the specialist.

In selecting a bonding method for plastics the key factors to consider are the function of the

parts, the environment in which they function, and the manufacturing process by which they are to be assembled.

Tables 3 and 4 are a good starting point to determine which assembly method or type of adhesive offers promise for the plastics you wish to join. The choice of assembly method can be further narrowed by considering the economic factors which would be involved to integrate the material into the manufacturing process.<sup>9</sup>

## TEST METHODS FOR ADHESIVES

Table 5 gives a list of useful test methods for evaluating the performance of joining methods on plastics. Most of the information was obtained from a list compiled by Rice.<sup>10</sup> See Volume 15.06 of the *Annual Book of ASTM Standards* for details of the test methods; see also Rice's Chapter 5 in this Handbook.

**Table 5. Test Methods for Plastic Bonding.<sup>10</sup>**

<i>Test Method</i>	<i>Description</i>
1. Tensile Tests	
ASTM D897	Test method for tensile properties of adhesive bonds
ASTM D1344	Cross lap tensile test
ASTM D2095	Tensile properties using bar and rod specimens
2. Shear Tests	
ASTM D4501	Block shear test method
ASTM D3163	Lap shear test for plastics
ASTM D3983	Thick adhered test method
3. Peel Tests	
ASTM D903	180° peel test
ASTM D1781	Climbing drum peel
4. Cleavage Tests	
ASTM D3807	Cleavage/peel test for engineering plastics
5. Adhesion	
ASTM D3808	Spot adhesion test
6. Adhesive-Plastic Compatibility	
ASTM D3929	Bent beam method for evaluating compatibility
7. Wetting Characteristics	
ASTM D2578	Wetting tension of plastic films

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# Bonding Textiles to Rubber

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When J. B. Dunlop made his first pneumatic tire in 1888, Irish flax was used as the reinforcing material. Cotton, however, quickly replaced flax because of material cost savings, and cotton was used in tires until World War II. It was used with no adhesive treatment since the mechanical interlocking brought about by protruding filament ends was enough to adhere cotton cord to the rubber. However, as tire performance requirements became more demanding it was necessary to use man-made fibers as reinforcing materials.

In the 1940s rayon was used almost exclusively in tires. It was difficult to adhere rayon to rubber mechanically because of the smooth surface of the rayon filaments. Fortunately, two Dupont Co. chemists, W. H. Charch and D. B. Maney<sup>1</sup> found that incorporating a resorcinol-formaldehyde thermosetting resin into a rubber latex made a cord adhesive which gave excellent adhesion of rayon to rubber carcass compounds. The same "RFL" cord adhesive was also used when nylon was introduced as a tire reinforcing material in 1947 and when glass fiber was introduced as belt material in belted bias and radial tires.

## RESORCINOL FORMALDEHYDE (RF)

The resorcinol molecule, like phenol, undergoes substitution at ring hydrogen positions. The two hydroxyl groups act as electron donors to the aromatic ring. This electron donating effect directs incoming substituents to the one *or-*

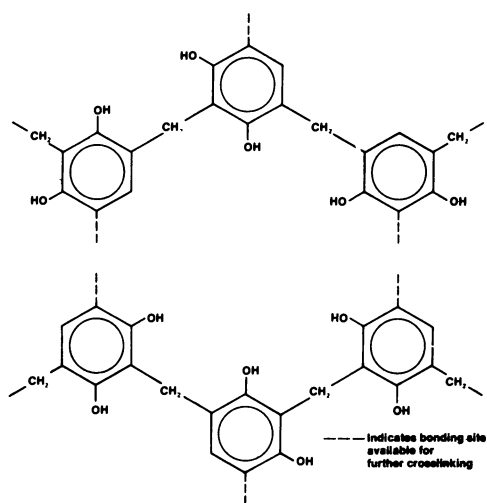


Fig. 1. Resorcinol-formaldehyde structures.

*tho* and two *para* positions. Resorcinol acts much more rapidly than phenol under similar conditions. The reaction product of resorcinol and formaldehyde can be represented as in Fig. 1.<sup>2</sup>

Depending on the molar ratio of the two reactants we can obtain products which range from syrupy liquids at low formaldehyde levels to completely crosslinked thermosetting resins at high levels of formaldehyde. *Novolaks* used in tire cord adhesive are RF resins of low formaldehyde content (mol ratio of resorcinol to formaldehyde 1.00/.40 to 1.00/.75) and are prepared under acidic conditions. These resins are manufactured and sold commercially as

**Table 1. Novolak RFL Dip Recipe.**

<i>Resin Solution</i>	<i>% Solids</i>	<i>Parts Dry</i>	<i>Parts Wet</i>
Penacolite R-2200	70	19.02	27.17
NaOH Solution	50	1.40	2.80
Formaldehyde	37	2.88	7.78
Water	—	—	267.29
Total Solids		23.30	305.04
Latex and Resin Solution			
Resin Solution (above)	7.64	23.30	305.04
Vinyl pyridine latex	41.00	100.00	244.00
		123.30	549.04
Total solids: 22.46 %			
F/R (dry): 15.14/100 parts			
Resin/latex (dry): 19.02/100 parts			

**Table 2. "In Situ" Resin Fabric Dip.**

<i>Resin Solution</i>	<i>% Solids</i>	<i>Parts Dry</i>	<i>Parts Wet</i>
Resorcinol	—	16.10	16.10
Formaldehyde	37	5.24	14.16
NaOH	50	1.26	2.52
Water	—	—	251.12
		22.60	283.90
Total solids: 7.96%			
Resin aged 6 hours at 23°C			
Latex and Resin Solution:			
Resin solution	7.96	22.60	283.90
VP latex	41.10	100.00	243.31
Water	—	—	17.68
		122.60	544.89
Total solids: 22.5%			
Age 18 hours at room temperature			

both liquids (70–75% solids) and dehydrated brittle solids. See Table 1.

*Resoles* are prepared in situ and then added to a rubber latex to be used as a cord adhesive. See Table 2.

## LATEX TYPE (L)

Natural and SBR latexes were first used in RFL adhesive systems. However it was found that latexes containing vinyl pyridine terpolymer (B/S/VP) gave high levels of adhesion of fibers to rubber. Fig. 2 illustrates the chemical composition of this latex.

The reason for this good adhesion has been a subject of speculation for some time. One explanation is the exceptionally high strength of the vulcanized terpolymer itself. Another attri-

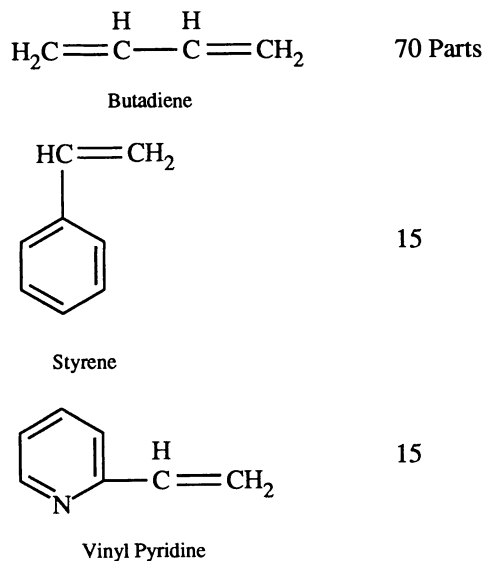


Fig. 2. Latex composition for FRL adhesive dips.

butes the superior adhesion to a direct dipole-dipole interaction between the more polar vinyl pyridine terpolymer and the textile fiber. A third view is that the pyridine nuclei facilitate the interaction of the resin and the rubber phase.

A typical Cord Processing Unit is shown in Fig. 3, where the fiber is dipped in RFL, dried at 150°C, and heat set at temperatures of 175–240°C.

## EVALUATION OF ADHESION

### Static Adhesion

Adhesion is represented by the force required to pull an embedded cord through and out of a rubber block in the H-Test, T-Test, and U-Test.<sup>3,4</sup> In these methods, the force is affected by the embedded length of the cord, the rate of loading, and the temperature of the test sample. Measurements are frequently made at 100–130°C, since temperature in a running tire may be this high. Fig. 4 illustrates these pull-out tests.

Adhesion of textile fabric to rubber is sometimes evaluated by stripping a two-ply specimen. The specimen, Fig. 5, consists of rubber-test fabric-inner rubber-test fabric-rubber. Again the sample may be tests at room temperature as well as any desired elevated temperature.



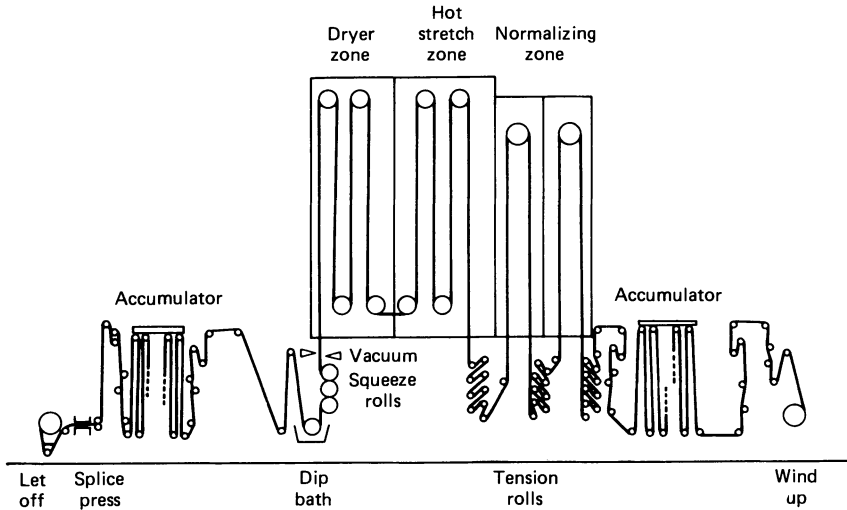


Fig. 3. Tire cord processing machine.<sup>47</sup>

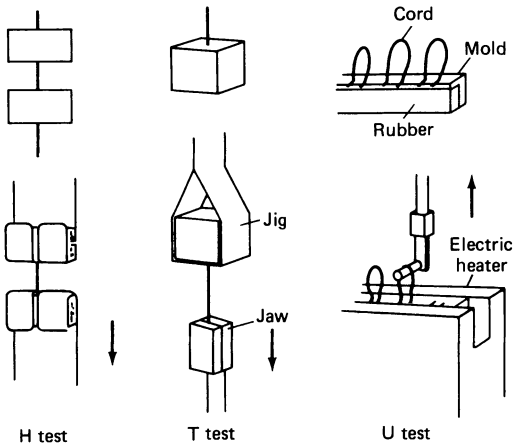


Fig. 4. Test specimens and testing features of pull-through type tests.<sup>47</sup>

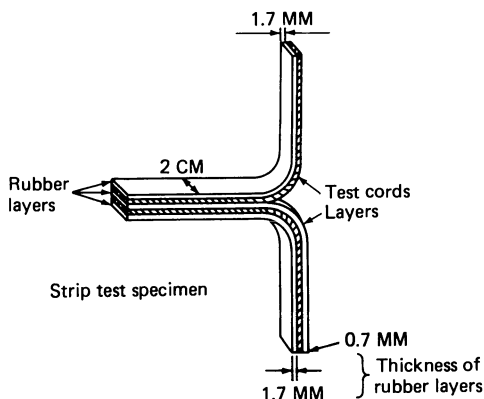


Fig. 5. Peel sample for testing fabric to rubber adhesion.

## FACTORS WHICH AFFECT ADHESION

In order to obtain maximum adhesion of dipped rayon or nylon to rubber compounds several factors must be considered.

### Effect of Formaldehyde-to-Resorcinol Ratio of RFL Adhesive

To obtain a high level of adhesion it is recommended that the formaldehyde-to-resorcinol mol ratio of the adhesive dip be in the range of 2:1 (Fig. 6).

### Effect of RF Resin-to-Latex Ratio on Adhesion

Adhesion can be affected by the resin-to-latex ratio in the adhesive dip. Too much resin in the adhesive can result in stiff cords with poor fa-

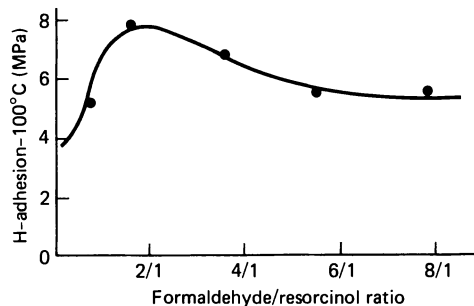


Fig. 6. Formaldehyde-to-resorcinol ratio of the adhesive dip—effect on adhesion.

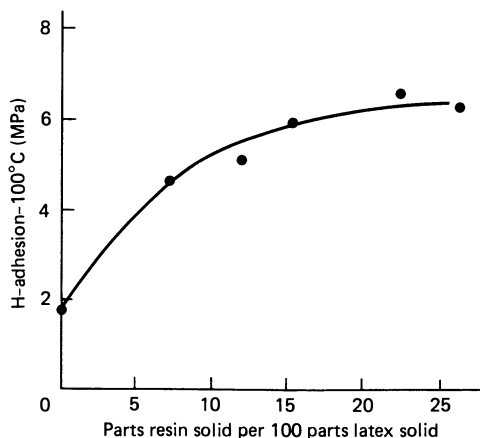


Fig. 7. RF-to-rubber solids in tire cord adhesives—effect on cord adhesion.<sup>47</sup>

tigue resistance, while too much latex can give unsatisfactory film strength and low bonding strength. A ratio of 1:4.5 to 1:6.0 RF to rubber solids as shown in Fig. 7 is considered optimum for most tire cords.

### Effect of RFL Dip Pickup

Generally bond strength increases with pickup of cord. About 4–6%, as shown in Fig. 8, is considered optimum for satisfactory adhesion of cord to rubber.

### Effect of RFL pH on Adhesion

Optimum cord adhesion is obtained at dip pH of about 9.5 when only sodium hydroxide is used in the dip recipe, while adhesion is not significantly affected at any pH over 8.0 when

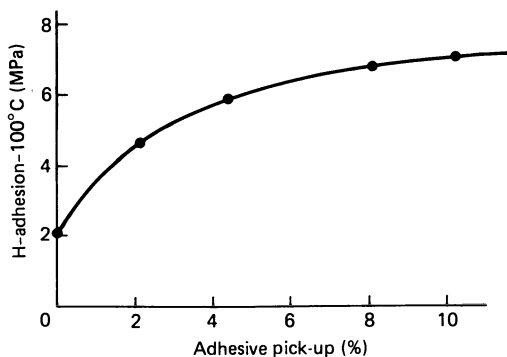


Fig. 8. Effect of RFL pickup on cord to rubber adhesion.

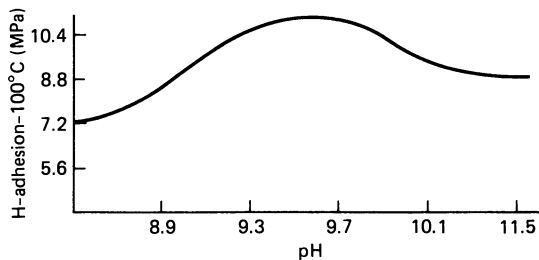


Fig. 9. Effect of RFL pH on tire cord adhesion to rubber.

ammonium hydroxide is used to catalyze the RF reaction (Fig. 9).

## THEORY OF RFL ADHESION

The nature of the fiber plays the most important role in RFL treatment of tire cords. We know that rayon and nylon cords are easy to bond to rubber by RFL treatment, but polyester cord is extremely difficult. This can be attributed to the nature and structure of the fiber.

There a number of opinions on how RFL functions with rayon and nylon. Rayon contains active OH groups on its polymer chain while nylon contains amide groups (CONH). Moults<sup>5</sup> suggests the formula in Fig. 10 for adhering of RFL to rayon. A similar possibility could exist with nylon. He suggests a chemical reaction between the methylol groups on the RF molecule and the active hydrogens on both rayon and nylon.

M.W. Wilson favors a dipole-dipole interaction between the RF resin and active groups on rayon and nylon. In his paper Wilson<sup>6</sup> dwells in depth on the potential of hydrogen bonds between RF and fiber surface. He pictures this occurring according to the structure in Fig. 11.

The question arises as to whether the adhesion mechanism between RF resin and rubber is one of mere physical entanglement or whether specific chemical interaction is involved as well. Dlugosz<sup>7</sup> has shown, by electron microscope examination of adhesive films, that the two phases of the adhesive remain discrete, and that the resin takes the form of a net which encloses the latex particle. He concluded that the adhesive functions principally by providing two mechanically interlocked phases,

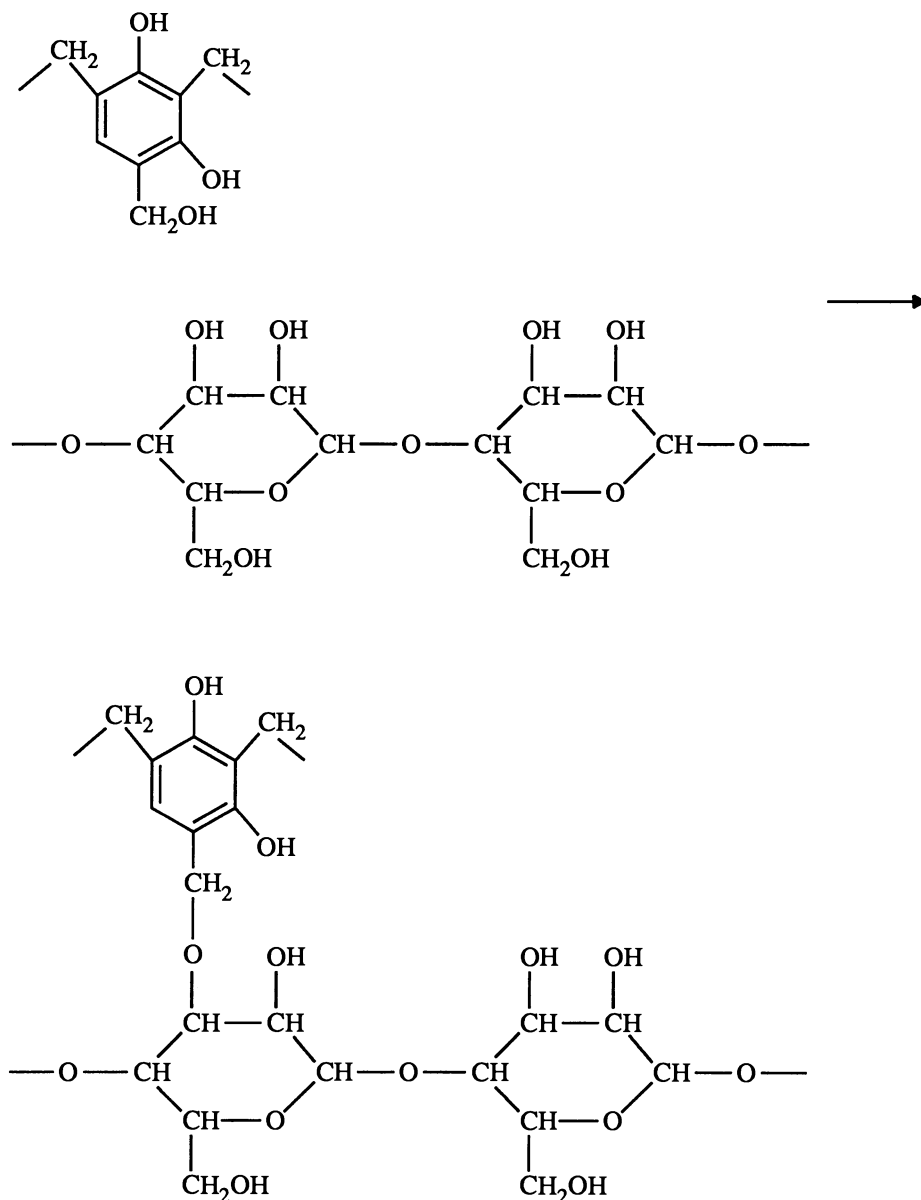


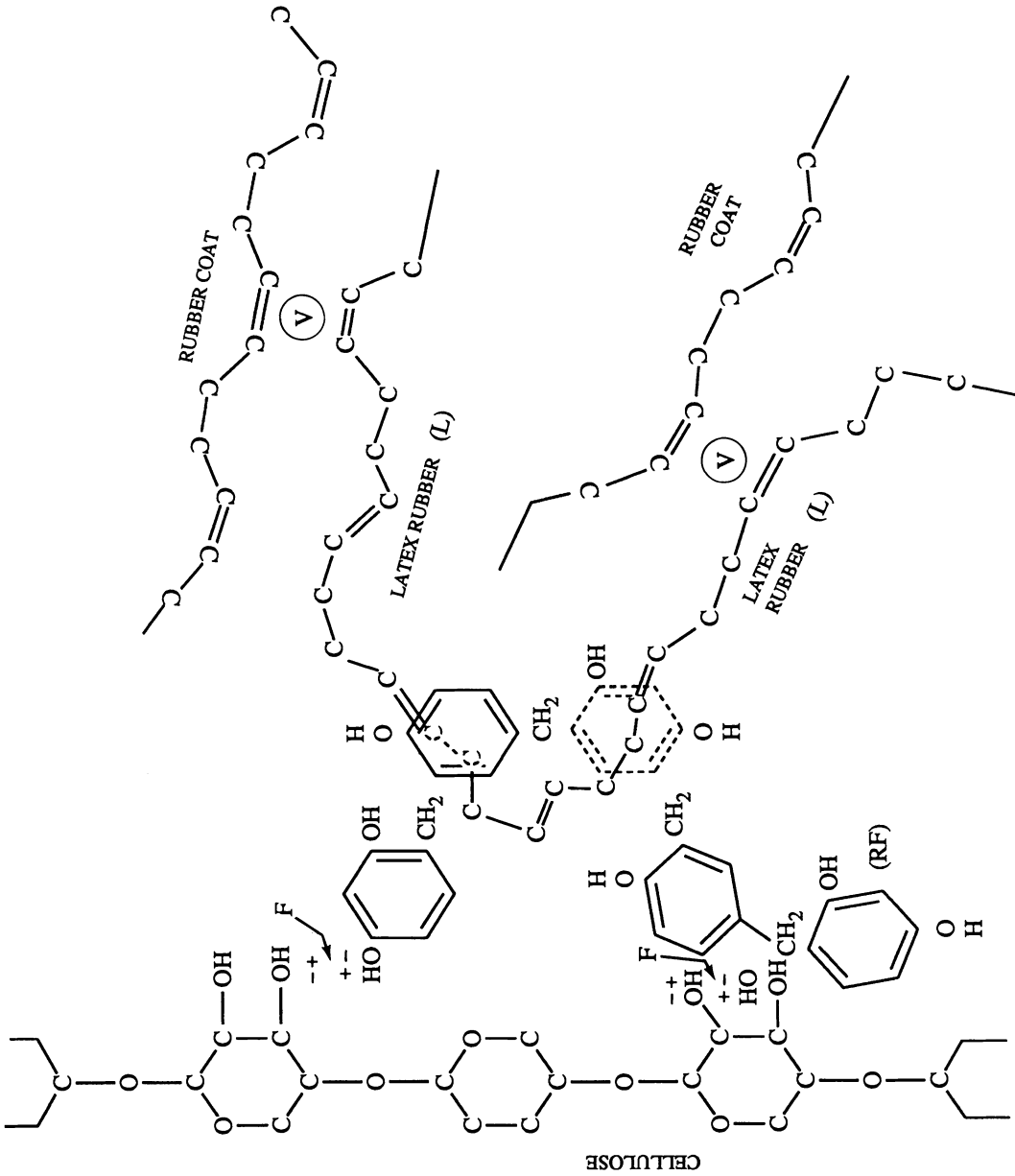
Fig. 10. Moul't's theory of adhesion of RFL to rayon tire cord.

each with separate affinities for the substrates which are being united.

On the other hand, it is well known that phenol-formaldehyde resins are able to vulcanize diene rubber. Two basic types of mechanisms have been postulated for this interaction. The first, associated with van der Meer,<sup>8</sup> involves the formation of a methylene quinone intermediate, formed from the methyloated re-

sorcinol, which reacts with an active hydrogen atom, such as the allylic hydrogen of the isoprene unit of natural rubber. The product after rearrangement is a benzenoid resorcinol nucleus having, in this instance, the rubber molecule attached to it (Fig. 12).

The second type of mechanism, associated with Greth,<sup>9</sup> suggests the formation of chroman structure between the benzene ring of the re-



F = dipole-dipole or H bond attraction. V = vulcanization bond.

Fig. 11. Rayon-RFL adhesion scheme according to Wilson.

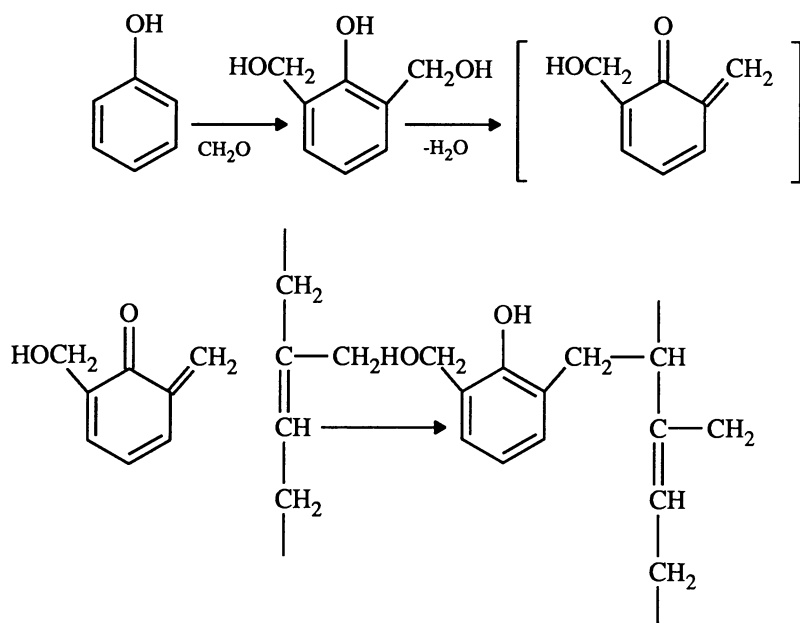


Fig. 12. Van der Meer's scheme for adhering RFL to rubber.<sup>47</sup>

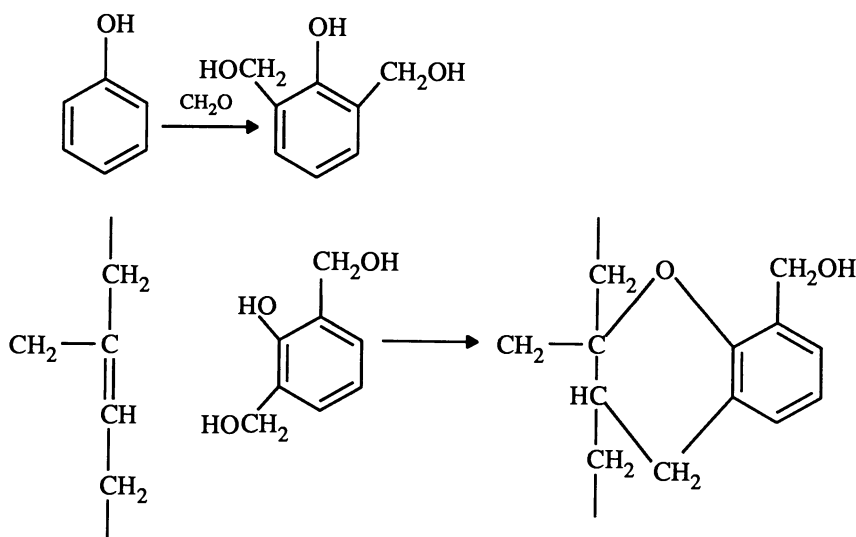


Fig. 13. Greth's theory for adhering RFL to rubber.<sup>47</sup>

sorcinol and the double bonds of butadiene units in the diene synthetic rubber. Fig. 13 illustrates this type of mechanism.

#### ADHESION OF POLYESTER TIRE CORD

There is practically no adhesion between polyester tire cord and RFL adhesive dip. Poor

adhesion may be due to reduced ability to form hydrogen bonds, lack of reactive hydrogen in the polyester molecule and its hydrophobic nature. One of the most important methods for adhering polyester to rubber requires a first treatment of the fiber with an *isocyanate* or a blocked isocyanate. The isocyanate,  $-\text{NCO}$ , has a specific action for both polyester and rubber. Polyester was first treated with dilute or-

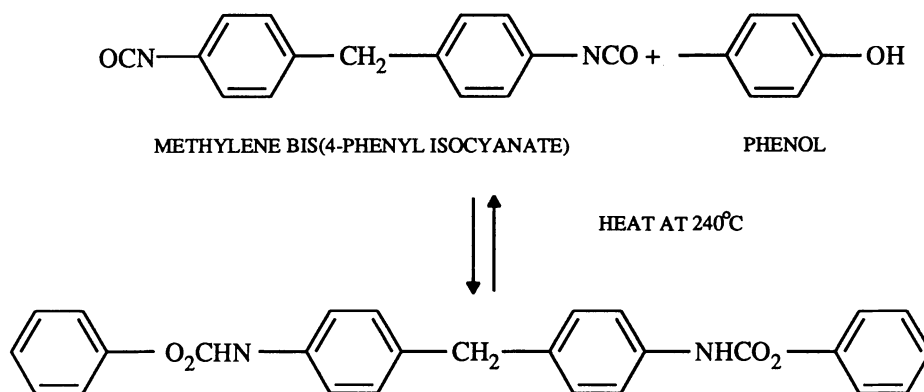


Fig. 14. Typical blocking-unblocking reaction.

ganic solutions of an isocyanate, and after drying given a second treatment of a standard RFL. However, the isocyanate-in-solvent treatment of polyester cord was never commercialized, except for V-belt cords, because of the need for solvent recovery, ventilation, and toxicity.

Isocyanates form addition products reversibly with compounds which contain moderately reactive hydrogen, such as phenol, oximes, lactams and malonates. Fig. 14 is an example of a typical blocking-unblocking reaction. These addition compounds, called "blocked isocyanates," are stable to water. They have been used in place of free isocyanate. The phenol-blocked isocyanates are the most common. In 1957 the DuPont Co.<sup>10</sup> developed an aqueous dip based on blocked isocyanate. This process, called D-417, used phenol-blocked methylene bis(4-phenyl isocyanate) and a water soluble epoxide, the reaction product of glycerine and epichlorohydrin. RFL is used as the topcoat or second step dip:

Hylene MP <sup>a</sup>	3.56 parts
Nagase 010A epoxide <sup>b</sup>	1.34
Aerosol OT	0.10
Water	95.00
	<hr/> 100.00 parts

<sup>a</sup>DuPont Co., no longer available. Blocked isocyanates are available from other companies.

<sup>b</sup>Nagase Co., Ltd., Japan.

The reaction of isocyanate and epoxide showed that the major product during cure of the D-417

dip was a polyurethane resin. The primary source of the hydroxyl for polyurethane formation is the epoxide resin.

The probability of a major role of the polyester group in reaction with dip chemicals during cure is quite low. The polyurethane-polyester bond is pictured primarily as a physical interaction rather than a chemical one. Iyengar<sup>11</sup> reported that the polyurethane from methylene-*bis*(4-phenyl isocyanate) and the epoxide have a cohesive energy density of 10.5. Polyethylene terephthalate has a cohesive energy density of 10.3. The compatibility between these two networks would be quite high and the probability exists for adhesion by the diffusion theory of Voyutskii.<sup>12</sup>

Figure 15 shows the effect of subcoat pickup on adhesion after a topcoat of RFL. Optimum subcoat pickup for both adhesion and economy is about 1.0%.

Heat set conditions for polyester tire cord are

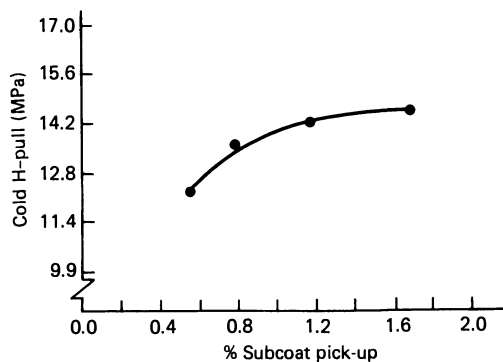


Fig. 15. Cold H-pull adhesion vs. subcoat pickup.

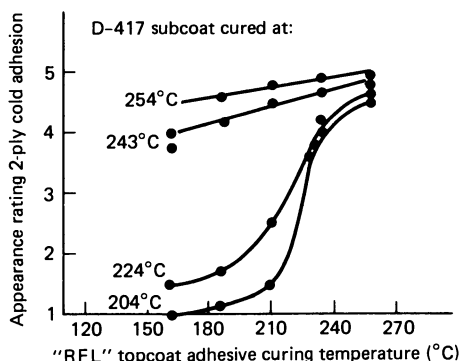


Fig. 16. Effect of curing temperature on polyester adhesion.

very critical in order to obtain maximum adhesion to rubber. A heat set temperature of at least 230–240°C is necessary to develop good adhesion of polyester to rubber compounds. Somewhat lower temperatures of 210–220°C are required for RFL topcoat heat set. Fig. 16 shows the effect of curing or heat set conditions on polyester adhesion using the D-417 two-step adhesive system. Heat set temperatures for the D-417 subcoat are shown within the graph structure, while heat set temperatures for the RFL topcoat are shown along the abscissa of the graph. Adhesion rating of 1 indicates poor adhesion while 5 shows excellent adhesion with 100% rubber coverage on the pulled polyester cord sample. This figure shows that high heat set conditions are necessary for both subcoat and topcoat adhesives in order to obtain optimum adhesion of polyester to rubber.

#### Pexul or H-7 Single-Step Adhesive Dip for Polyester

One of the first single-step adhesive dips for polyester was developed by ICI.<sup>13</sup> This adhesive was based on a co-resin of resorcinol and

Table 3. Pexul Polyester Single-Step Adhesive Dip.

Component	Parts by Weight
Koppers Penacolate R-2200 resin (70%)	3.4
Sodium hydroxide	0.17
Water	18.8
Pexul (20%)	30.0
Vinyl pyridine latex (38%)	31.8
Water	12.6
Formaldehyde (37%)	1.0
Water	1.0
	98.8

*chlorophenol* with formaldehyde. The reaction mechanism for resin formation is shown in Fig. 17 while the actually dip recipe is illustrated in Table 3.

Many other one-step adhesive dips for polyester fibers have been patented over the last 15 years. The adhesion activating agents in the RFL dip are usually based on isocyanates or *cyanurates* such as triallyl cyanurate, triphenyl cyanurate, etc. Other agents are also used based on condensation polymers similar to that used in Pexul. A more detailed discussion on this subject is given in *Rubber Chemistry and Technology*, Vol. 58, No. 3 (1985).

#### Chemical Activation of the Polyester Surface During Fiber Spinning

An important development in polyester technology occurred when Fiber Industries Inc.<sup>14</sup> activated the surface of polyester filaments during the actual melt spinning of the fibers. It was then only necessary to apply a single topcoat of standard RFL for optimum adhesion of fiber to rubber. The undrawn filaments as formed in the spinning process were dipped in a finish solu-

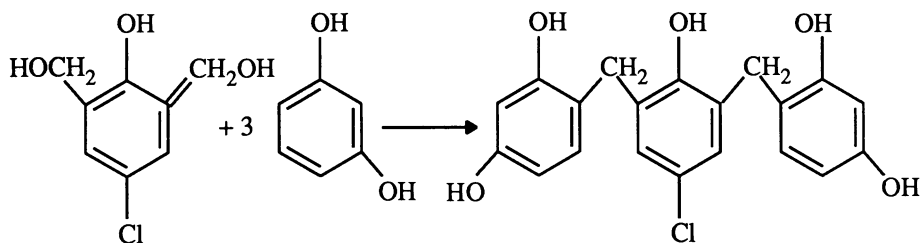


Fig. 17. Reaction mechanism for active ingredient in Pexul cord dip.<sup>47</sup>

**Table 4. Composition of Finish Solution Used to Activate Polyester Fiber Surface During Spinning.**

0.1 % sodium carbonate
5.0 % glycidyl ether made from epichlorohydrin and glycerine (epoxide equivalent 140–160)
5.0 % spin finish containing approximately 60 % dimethylsiloxane
5.0 % spin finish containing 75 % ethoxylated sorbitan monooleate (20 moles polyoxyethylene) and 25 % ethoxylated octylphenol (12 moles polyoxyethylene)
84.9 % water

tion which had the composition given Table 4. The dipped filaments were then drawn at high temperatures in order to heat set the adhesive onto the cord.

Subsequently numerous other attempts were made to activate the surface of polyester fibers during the melt spinning operation and thus eliminate the necessity for double dipping the cord. Most of these cord finishes were based on epoxides and silanes. Again blocked isocyanates and cyanurates were popular additions to the fiber finishes during melt spinning.

### ADHESION OF GLASS TIRE CORDS TO RUBBER

Some glass tire cord is still being used in the belts of belted-bias and radial passenger tires. However, the use of glass in belts has been limited because of the preference of steel wire in radial tires. Still, there has been some research work done in order to improve the dynamic performance of glass belts in tires.

A significant development was disclosed by Lin.<sup>15</sup> He replaced part of the vinyl pyridine terpolymer latex in the adhesive recipe with polybutadiene latex. Glass cords dipped in this polybutadiene latex adhesive were more resistant to fracture under cold weather conditions. This was attributed to the lower  $t_g$  of polybutadiene compared to vinylpyridine-styrene-butadiene rubber.

### ARAMID ADHESION

One of the most significant developments in fiber technology over the last fifteen years was the introduction of aromatic polyamides as rub-

ber reinforcement materials. Aramid fibers have been engineered for the reinforcement of radial tires and mechanical goods, including hoses, conveyor belts and power transmission belts.

These high strength fibers are prepared according to the methods described in the 1971 U.S. Patent issued to S. L. Kwolek.<sup>16</sup> Solutions of polybenzamide and poly(*p*-phenylene terephthalamide) exhibit liquid crystal properties. When these polyamide solutions emerge from a spinneret they have almost perfect molecular orientation, and the emerging fibers, therefore, have a very high orientation of polymer molecules. The resulting fibers are very strong in comparison to other fibers. Iyengar<sup>17</sup> discusses in detail the mechanism for adhesion development of aramid fibers to rubber. Thermodynamic compatibility of the substrate and adhesive was shown to be a key requirement for promoting bonding to the aramid surface. Such compatibility is attained when the solubility parameters ( $\delta$ ) of the substrate and adhesive are matched. Iyengar<sup>17</sup> also proposes a two-step adhesive for aramid fiber adhesion to rubber. The first step or subcoat would consist of the composition shown in Table 5. An RFL topcoat based on preformed RF resin is then used as the second-step dip (Table 6).

Most of the aramid adhesive systems initially used were based on a first-step dip of either an epoxide or a blocked polyisocyanate and then a second or top coat of RFL. Wenghoefer<sup>18</sup> in his patent disclosed a somewhat different first step dip which consisted of bis( $\beta$ -azido-formyl oxyethyl)isophthalate. After drying, the cord thus treated, was then dipped in a phenolic adhesive and cured at 230°C for 60 seconds. A patent issued to Van Gils<sup>19</sup> uses a one-step dip based on vinyl pyridine latex, trimethylolphenol, resorcinol-formaldehyde resin, and

**Table 5. Composition of First Step for a Two-Step Adhesive for Aramid Fiber Adhesion to Rubber.**

Nagase NER 010A (epoxide) <sup>a</sup>	2.22 parts
10 % Sodium Hydroxide	0.28
5 % Aerosol OT <sup>b</sup> (75 % solids)	0.56
Water	96.94
Total	103.06 parts

<sup>a</sup>Nagase Co., Ltd., Japan

<sup>b</sup>American Cyanamid Co.



**Table 6. Composition of Second-Step Dip for a Two-Step Adhesive System for Aramid Fiber Adhesion to Rubber.**

	<i>Parts</i>	
	<i>Wet</i>	<i>Dry</i>
Water	141.0	
I. Ammonium Hydroxide (28%)	6.1	
Preformed RF resin (75%)	22.0	16.5
II. Vinyl pyridine latex (41%)	244.0	100.0
Water	58.0	
III. Formaldehyde (37%)	11.0	4.1
Water	58.0	
IV. HAF black dispersion (25%)	<u>60.3</u>	<u>15.1</u>
Total	600.4	135.7

water. Elmer,<sup>20</sup> in a patent issued to General Tire & Rubber Co., uses an aqueous adhesive composition of phenol-aldehyde resin and a vinyl pyridine latex. Treatment is preferably repeated three times. Other adhesive treatments for aramid fibers will undoubtedly be developed in the future as its use expands as a rubber reinforcement element.

#### EFFECTS OF ATMOSPHERIC POLLUTANTS ON ADHESION OF RFL COAT TIRE CORDS TO RUBBER

The adhesion of RFL-coated tire cords to rubber can be adversely affected if the dipped cords are exposed to ozone, UV light, nitrogen oxides, sulfur dioxide, or air before vulcanization into rubber. Iyengar<sup>21</sup> proposed that ozone exposure of RFL reduces adhesion because ozone attacks the double bonds of the butadiene component of the rubber latex and impairs its co-curing with the solid rubber compound. Infrared studies by Solomon<sup>22</sup> reinforced this argument. When typical RFL films were exposed to ozone, the IR spectrum showed an increase in IR absorption at  $1720\text{ cm}^{-1}$ , corresponding to an increase in the carbonyl content in the exposed film. An RFL film with no ozone exposure did not show this absorption at  $1720\text{ cm}^{-1}$ . The increased carbonyl content is due to the reaction of some double bonds in the rubber with ozone and therefore, would leave fewer unsaturation sites for rubber crosslinking and adhesion.

The synergistic effect of humidity and ozone is demonstrated with nylon, rayon, and polyes-

ter tire cords<sup>22</sup> in Fig. 18. At the same ozone level, adhesion of exposed cords to rubber decreases as the humidity level increased during exposure. Several methods have been proposed in order to reduce the adverse effects of atmospheric exposure. Encapsulation of the rubber latex particles helps prevent the reaction of ozone with diene rubbers.<sup>23</sup> Polymers of methyl methacrylate, acrylic acid, and N-methylol acrylamide are added to RFL for use as cord dips for rayon, nylon, and polyester tire cords. Adams<sup>24</sup> added N,N'-ethylene-bis-stearamide to tire cord adhesives in order to reduce the adverse effects of atmospheric pollutants. Microcrystalline waxes<sup>25</sup> and/or Fischer-Tropsch waxes can be added to adhesive dip formulations in order to minimize the loss of adhesion to rubber when the cords are processed in fuel oil or kerosene-heated dryers. A most important factor in preventing adhesion losses of dipped RFL fabrics is to wrap the dipped fabric rolls immediately with layers of heavy kraft paper and cardboard. This prevents direct exposure of the fabric surface to atmospheric degradants and in most cases will prevent excessive adhesion losses.

#### RUBBER ADHESION TO BRASS-COATED STEEL WIRE

The performance of steel belted tires, as with tires reinforced with other fibers, is dependent to a large extent on the adhesive bond between the tire cord and the rubber in the skim stock surrounding the cord. The use of a thin brass layer on steel tire cord is the major adhesive

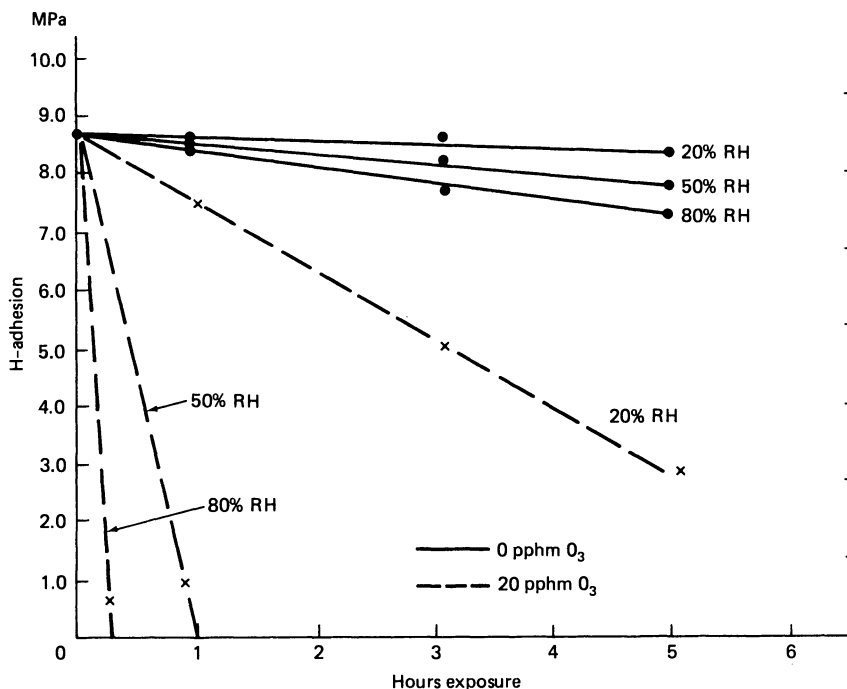
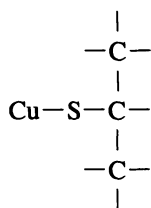


Fig. 18. H-adhesion losses—1680/2 nylon at different levels of humidity and ozone at 30°C.

for bonding steel cords to rubber. The mechanism of rubber-brass adhesion has been the topic of much speculation and fundamental research for years, and sophisticated instruments have been used for the analysis of steel cord surfaces and the rubber-brass interface.

### Nature of the Rubber-Brass Bond

Sanderson<sup>26</sup> discovered the adhesion of brass to sulfur-vulcanizable rubber over 100 years ago. Interest in the mechanism of this bond formation has been spurred on by the advent of the steel-belted radial tire. Buchan and Rae<sup>27,28</sup> postulated that chemical bonds are formed between copper atoms on the brass surface and sulfur atoms of crosslinked polymer molecules:



Van Ooij<sup>29-31</sup> was the first to apply XPS (X-ray photoelectron spectroscopy) to the analysis

of steel cord surfaces and rubber-brass interfaces. He observed that an interface film of reactive products is always formed. By means of the chemical shift principle he identified the species Cu<sub>x</sub>S, ZnS, and ZnO as the constituents of this film, with Cu<sub>x</sub>S always on top. He postulated that Cu<sub>x</sub>S, a nonstoichiometric type of copper sulfide, acts as the adhesive which bonds the metal to rubber through a catalytic effect on the vulcanization reaction.

However, van Ooij<sup>32</sup> claims that there is now direct evidence that chemical bonds do not exist between the Cu and rubber. This was shown in an experiment where milling of Cu<sub>x</sub>S into rubber showed no reinforcement effect and therefore no adhesion to the polymer. Van Ooij says that the important criteria for good bonding are whether Cu<sub>x</sub>S is formed or not, its cohesive strength, its adhesion to the substrate, which consists of brass still covered with ZnO. Also important is the ZnO which has been partly converted to ZnS as well as the rate of secondary corrosion reactions which proceed underneath the Cu<sub>x</sub>S film once it has been formed. The schematic of oxide film on brass coated steel is depicted in Fig. 19.

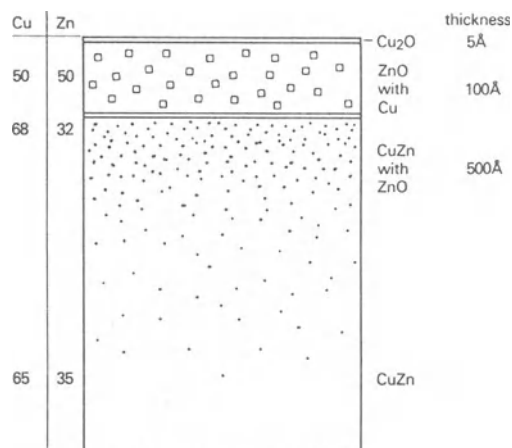


Fig. 19. Schematic of oxide film on brass-coated steel cord.<sup>48</sup>

In van Ooij's model, brass develops a high bond strength to rubber because the sulfide not only has good adhesive and cohesive properties, but is also very porous so that the rubber molecules become entangled in this film during vulcanization. This phenomena is depicted in Fig. 20.

### Effect of Brass Composition and Plating Weight on Brass Reactivity and Adhesion

The first in-depth study on the effect of coating properties was done by Maeselle and Debruyne.<sup>33</sup> They studied the effects of brass-copper content, variations of plating conditions

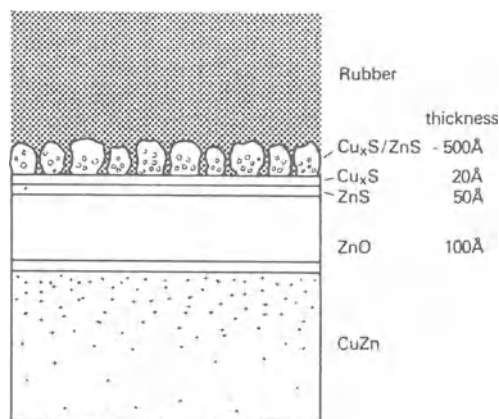


Fig. 20. Schematic of interfacial sulfide film in rubber-brass bonding showing mechanical interlocking.<sup>48</sup>

leading to different brass grain size, plating weight, mechanical deformation of the electrodeposit, thermal treatments, and compound composition. The optimum copper content of the brass coating at constant plating weight was reported to go through a maximum which could be 60%, 67–70%, or 75% copper depending on the rubber compound used in adhesion testing. They reported that adhesion was optimum for most rubber compounds when the brass coating thickness was in the 0.2  $\mu\text{m}$  range and the copper content in the brass was 68%. Today most of the wire used in the rubber industry for reinforcement in tires has a brass coating thickness of about 0.2  $\mu\text{m}$  and a composition of approximately 70% copper and 30% zinc.

### Other Factors Affecting Adhesion of Rubber to Brass Coated Steel Wire

**Rubber Compound Effects.** Buchan<sup>34</sup> reviewed natural as well as synthetic rubber compounds and their adhesion to brass. However, compound studies are to some extent largely empirical because of the complexity of the different compound systems used in the rubber industry today. One can, however, draw several conclusions from the many adhesion studies made to date.

1. *Sulfur* is very important in the bonding reaction. The minimum sulfur loading for good bonding is about 2 phr. Generally sulfur-to-accelerator ratios of over 4 to 1 give high adhesion values.

2. *Sulfenamide*-type accelerators are commonly used in the rubber industry for rubber-brass bonding. Bertrand's<sup>35</sup> study showed that N-cyclohexyl-2-benzothiazole sulfenamide (CBS), N-*t*-butyl-2-benzothiazole sulfenamide (TBBS) and N,N-dicyclohexyl-2-benzothiazole sulfenamide (DCBS) all gave high bond strengths. The ultra-accelerators such as tetramethyl thiuram disulfide (TMTD) and tetramethyl thiuram monosulfide (TMTM) in small amounts or in combination with sulfenamides gave very low bond strengths.

3. Hicks, Lyon, Chirico, and Ulmer<sup>36,37</sup> made a comprehensive study of *carbon black* loadings and properties on adhesion. Pullout force increases with black loading, and reached an optimum at 50–60 phr. It appears from this

and other studies that the effect of carbon black properties and loading can be interpreted as being a mechanical one.

4. *ZnO* and *stearic acid* are important ingredients in all rubber compounds. Carpenter<sup>38</sup> made a statistical study on the effect of *ZnO*. *ZnO* loadings of 2, 5, and 8 phr were compared. It was reported that average particle size was most important for optimum adhesion. Hicks<sup>39</sup> reported an optimum content of 15 phr *ZnO*. Conflicting results such as these have also been reported by others and most probably indicate that the effect of *ZnO* is dependent on the other ingredients in the rubber compound. It is known<sup>40</sup> that *stearic acid* is converted into zinc stearate during the initial stages of the cure. However, there are so many factors affecting zinc stearate formation that it is difficult to access its affect on rubber adhesion.

5. *Antioxidants* used in the rubber industry do not exert any great effects on rubber-brass adhesion.

### Adhesion Promoters for Rubber-Brass Adhesion

Most of the tire companies used cobalt salts and/or a variation of the HRH system in their steel cord skim compounds.

**Cobalt Salts.** Barker<sup>41</sup> studied the effects of cobalt stearate, cobalt naphthenate, and a proprietary boron-containing metal-organic complex on adhesion to brass. He concluded that, with properly optimized compounds, little or no benefit is obtained from the use of cobalt insofar as initial adhesion is concerned. All salts, however, improved steam-aged adhesion to some extent. Other studies tend to support these claims.

**HRH Systems.** A review of currently available bonding agents such as HRH and modifications thereof, is given by Weaver.<sup>42</sup> HRH designates the use of *hexamethylenetetramine* (hexa), *resorcinol*, and a *hydrated silica* as additives to rubber in order to improve adhesion to brass coated wire. Normally about 1.5 phr hexa, 2.5 phr *resorcinol*, and 15 parts of silica are added to a wire skim stock. Pre-

formed resins such as *resotropin* (a precondensed *resorcinol-formaldehyde* resin), as proposed by Cunningham and Hart,<sup>43,44</sup> or *Penacolite Resin B-18* from Koppers Co.,<sup>45</sup> which react with hexa can also be used for bonding rubber to wire.

Results obtained by Van Ooij in his ESCA studies on the composition of interfaces between rubber and brass<sup>46</sup> confirm that cobalt salts and HRH form essentially the same interfacial products with a standard brass surface. Therefore, the mechanism of brass-rubber bonding must be the same for both bonding systems and differences in adhesion values must be explained by a modification of rubber properties (crosslink density, cure rate, modulus, etc.) or the rate of brass attack. Clearly, adhesion of brass to HRH-NR compounds cannot be explained on the basis of hydrogen bonds with the substrate, as in rubber-to-textile bonding.

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# Wood Adhesion

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## INTRODUCTION

The bonding of wood dates back to the ancient Egyptian Pharaohs, for whom artistic inlaid wood veneers, bonded with animal glues, were created by skilled artisans for the purpose of adornment. Today bonded wood products serve as a major structural component of shelter and furnishings, which continue to be cherished for aesthetic in addition to practical purposes. Wood bonding technology has evolved into a complex interdisciplinary science involving fields of chemistry, engineering, and materials science as well as wood science and wood technology. The size and shapes of wood to be bonded are limited only by man's imagination, ranging from microscopic fibrous material in hardboard to huge structural laminated members. The adhesives are no longer primarily animal glues but rather synthetic polymeric resins formulated and characterized with the assistance of state-of-the-art chemical instrumentation.

The challenges and opportunities for wood

bonding are derived by the nature of the interaction of the substrate with the resin. Because wood is a dimensionally anisotropic and chemically heterogeneous substrate, its properties are strongly influenced by climatic conditions such as temperature and humidity. The properties of composites made from wood components are also influenced by wood particle size and geometry, and by manufacturing process variables. The unique ability to manipulate the resin system's chemistry allows for the desired marriage of wood and adhesive, resulting in a successful bond and a useful wood/adhesive composite. The following sections will outline the nature of the challenges and opportunities apparent in a variety of products encountered in modern wood bonding applications.

## ADHESION TO WOOD

### Mechanisms for Adhesion in Wood Composites

Several common thermodynamic and kinetic parameters are involved in the process of bond formation. The adhesive may be applied either

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as a liquid or dried powder. If applied as a powder, the adhesive will become liquid upon the application of heat during processing. During the initial stages of bonding the liquid resin must be of controllable viscosity so it can flow across the microscopically rough surface typical of wood, penetrate and fill voids within the surface, and fill gaps between the substrates to be bonded. The adhesive mobility is insured either by heating, solvation, or both.

The mobile adhesive wets and then penetrates and absorbs into the wood fibers. Strong attractive forces are necessary for the adhesive to displace contaminants and adhere to wood fibers. The solvent, if present, will typically wet and absorb into the fibers at a greater rate than the adhesive polymer, leaving most of the adhesive resin concentrated at the wood interface and first few cellular layers. Bonding problems can occur if too little or too much adhesive flows into the wood.

Pressure and heat are applied in the process of curing a thermosetting adhesive resin. The resin viscosity typically decreases initially in a thermoplastic response to the heat. The viscosity then increases in response to crosslinking of the polymer molecules in the resin, the kinetics of which are influenced by heat. The resin becomes solid and the heat and pressure are removed as the process is completed. The duration of the thermoplastic phase controls the amount of flow into the wood and must be carefully manipulated for each process. In the case of bonding at ambient temperatures, such as in lumber laminating, the resin is typically catalyzed chemically and cured under pressure.

Solvent loss influences adhesive cure in addition to chemical crosslinking. The presence of excessive solvent can result in too much flow and resin overpenetration or *strike-in*. Too little solvent can result in too little flow and glue-line *dryout*. The rates of solvent loss and crosslinking increase with heat, however each rate increases differently with temperature.

The actual bonding between the adhesive polymers and the wood polymers is attributed to a combination of three mechanisms: mechanical interlocking, physical attraction, and covalent chemical bonding. The relative importance of these three mechanisms is still the subject of debate among adhesive chemists.

**Mechanical Interlocking.** Adhesive polymer and porous wood fibers invariably intertwine both microscopically and molecularly to form mechanical interlocks when an adhesive spreads, penetrates and wets a wood surface. The contribution of these interlocks to adhesive bond strength is not easily isolated and measured. Adhesive must penetrate beyond damaged fibers at the wood surface. Penetration two to six fibers deep into the wood and penetration of fiber walls on a molecular scale are generally thought to be necessary for durable structural bonds. This penetration may be necessary to provide added surface across which other bonding mechanisms can act, to mend submicroscopic fractures, or to provide a transition zone having mechanical properties intermediate to those of adhesive and those of the wood.

**Physical Attraction.** Physical attraction between wood and adhesive polymers can occur from van der Waals forces and hydrogen bonds. This physical adsorption (specific adhesion) can be quite strong, especially the hydrogen bonds between polar hydroxy groups on fiber-wall carbohydrates and adhesive polymer. Many adhesive chemists consider physical attraction to be the primary bonding mechanism. It is certainly exceedingly important as a first step in the formation of wood-adhesive interfaces, accounting for solvent wetting and adhesive polymer absorption into cellular wall fibers.

**Chemical Bonding.** Covalent chemical bonds between wood fiber and adhesive through the sharing of electrons is probable in crosslinking adhesive systems. However, the presence of such bonds may not be essential to waterproof adhesive bonds. Intermolecular physical attractions are sufficient for waterproof adhesive bonds.

### Factors Influencing Bond Formation

The bonding of an adhesive to wood fibers is a balance of several common thermodynamic and kinetic parameters and their interaction. A deficiency in these or any other aspect of the bond formation can result in a composite with unsatisfactory quality. Wettability is a necessary condition for adhesion and is preliminary to ad-

hesive penetration and diffusion, but good wetting does not assure good bonding. Adhesive distribution and adhesive properties strongly influence the final bonded product. Wood bulk properties and surface properties also influence the interaction of adhesive and substrate.

**Wettability.** Good wetting is synonymous with intimate molecular contact between adhesive and wood substrate, which must be compatible for good adhesion. Thermodynamic estimates of the surface free energy of wood are difficult because these are primarily nonequilibrium values due to the wood's swelling and change in wettability with time, particularly when water is the solvent. Contact angle measurements are rarely performed at the temperatures used in actual bonding and then with great difficulty. Wood properties such as extractives, density, porosity, and related differences in roughness influence measured values. The presence of nonpolar extractives, aging of the surface, and heating and drying of the wood fibers all tend to decrease surface energy and wetting.

Lignin is likely somewhat less wettable than carbohydrates when exposed to polar solvents, due to differences in their ability to interact with hydrogen bonding solvents. Wetting between solidly attached fibers and adhesive must occur for good adhesion. Because of the ability of aqueous caustic and aqueous phenol to swell and dissolve components on the wood surface, poor wetting is rarely a limitation with these adhesive systems.

**Diffusion and Penetration.** Thermosetting condensation polymers such as phenol-formaldehyde and urea-formaldehyde resin systems generate water as a byproduct of cure. If water also is the solvent, it is a requirement that the solvent water diffuse into the wood to lower the concentration of water at the interface which might otherwise inhibit cure. Water, or other solvent(s) if present, will carry mobile lower molecular weight polymer fractions into the cell interstices and cell walls. This "chromatographic" effect is the initiation of penetration.

If spray dried or other non-solvent-borne adhesives are involved, or after the solvent has

evaporated or diffused away from the glue line, penetration is completed during the thermoplastic phase of cure rheology. Wetting and diffusion must also take place during the thermoplastic interval when pressure and heat cause the adhesive to become fluid. Gelation of thermosetting adhesives immobilizes the adhesive polymer. The amount of diffusion and penetration prior to gelation determines if there is enough gap filling, enough or too much cellular penetration, and enough residual polymer at the site of the interface for good bond formation.

Because wood is hygroscopic, its moisture content is strongly subject to ambient temperature and relative humidity. The ability of the wood substrate to pick up or lose moisture after drying will in turn influence the rate and magnitude of solvent diffusion, particularly in waterborne adhesive systems. Water will also extend the thermoplastic phase of cure rheology. Manipulation of the resin's hygroscopicity and cure characteristics provide the basis for matching the seasonal diffusion/penetration needs with a resin's performance in a wood composite manufacturing facility.

**Adhesive Distribution.** The adhesive is frequently applied as a continuous film in plywood and laminated lumber using roller spreaders and curtain coaters. Spray applications rapidly are becoming the standard for construction plywood. Particle, flake, and fiberboards are spot welded by small amounts of adhesive, relative to surface area, applied as liquid droplets with spray nozzles or applied as powder particles with a molten slack wax or wax emulsion to temporarily bind the powder particles to the wood surface.

The ideal resin distribution for a particle-board manufacturer is usually defined by the maximum board properties obtainable when using a given minimal amount of adhesive. The cost of a continuous film of adhesive becomes prohibitive as wood particle size decreases in a composite because of the enormous wood surface area involved. How to obtain and measure the ideal resin distribution is subject to debate. Wood particle geometry, amount of adhesive applied, adhesive application method, spray



nozzle configuration, adhesive droplet or particle size, and adhesive surface tension all influence distribution.

Although an ideal adhesive distribution is difficult to define, bonding problems often can be traced to nonideal adhesive distribution. Bonding problems occur when excessive adhesive is captured by either coarse or fine particles. If some particles capture no adhesive resin at all, bonding problems can be more dramatic. Inefficient blending can reduce the strength of composites because individual flakes or particles receive little or no adhesive. Increased resin application rates can frequently compensate for inefficient blending, but at an additional raw material cost to the composite manufacturer. Screen fractionation and determination of adhesive distribution from one particle size to another has assisted in identifying distribution problems, and in the design of adhesive/wood blending systems.

**Adhesive Properties.** Adhesive performance depends on its ability to flow, wet, and penetrate the fiber walls, and to cure within prescribed temperature and time limits. The cured adhesive must have enough cohesive strength to impart the desired physical strength properties to the composite. Insights into the effects of formulation variables on resin cure rheology are gained with the aid of state-of-the-art as well as simple instrumental and observational methods.

The chemical composition of adhesive resins may be characterized spectroscopically by nuclear magnetic resonance in either the liquid or cured state. Infrared and ultraviolet methods are also applicable. High pressure liquid chromatography (HPLC) will characterize the low molecular weight fractions of resins while gel permeation chromatography (GPC) will characterize the high molecular weight fractions. GPC may be coupled with a laser light scattering photometer for absolute molecular weight measurements.

Cure rate may be characterized by gel times and stroke cures, and more quantitatively with a differential scanning calorimeter (DSC). Dynamic mechanical analysis (DMA) and torsional braid analysis (TBA) may be used to

characterize cure rheology. Fracture mechanics may be used to characterize physical strength properties of either the cured resin or the composite.

The techniques mentioned above are but a few of the tools useful in characterizing a resin's properties, so that its properties may be more closely matched to the requirements of the final product.

## Wood as a Substrate

**Surface Structure and Texture.** Wood surfaces are rough at the microscopic level. The roughness is caused by the inherent anatomy of the wood and the method of surface preparation.

Wood is structurally composed of fiber shaped cells. The surface texture varies from species to species, hardwoods to softwoods. In addition to grain orientation that results from the fibrous nature of wood, different types of wood occur within a tree. Juvenile wood is formed during the first years of a tree's life and is composed of relatively short fibers. The heartwood of a tree differs chemically from the sapwood. Annual growth consists of alternating rings of springwood and summerwood, each differing in density and porosity. All these factors account for differences in texture as well as permeability, density, and compressibility.

The preparation of the wood for composite manufacture involves some combination of sawing, planing, milling, thermomechanical pulping or other machining which increases surface roughness. The result is torn fibers, exposed cell lumina, and, in general, gross irregularities which can hinder good adhesive bonding.

Adhesive penetration to undamaged fibers is necessary for anchoring. Pressure is needed during processing to assure good wood-to-wood contact, and also to contain the steam formed by the water that is the byproduct of condensation in the case of phenolic and amino resins. The wood-to-wood contact must be nearly intimate and the gluelines must be thinner than the diameter of a fiber for durable adhesive bonds. Because of the variety of wood shapes used in bonding, from small fibers in fiber-

board to lumber in laminated lumber, the range of machining and milling techniques is great. But all have at least one common need: proper maintenance of wood reduction and surface preparation equipment will help to minimize problems further down the production line.

### Chemical Composition of the Surface.

Wood surfaces are as heterogeneous chemically as they are texturally. Three bulk surfaces are exposed when a fiber is cut open. These are the cell cavity, the severed cell wall and the middle lamella or the bonding area between individual fibers. The cell wall accounts for the greatest volume of material, but the chemistry of each of the layers can become critically important in a given bonding situation.

The fibers of wood are analogous to reinforced concrete. Oriented cellulose polymer molecules compose microfibrillar strands. These are encased in a sheath of other carbohydrate polymers. A continuous network of amorphous phenolic lignin polymer interpenetrates the carbohydrate frame and bonds it together. Numerous hydroxy groups are available for hydrogen bonding in the carbohydrates making them highly polar. Because lignin is an alkylated phenolic, it is less polar but still may provide additional reactive sites on the phenolic ring. The lignocellulosic matrix is present in significant quantities wherever a fiber is cut. In addition, an assortment of metabolic by-products and protoplast residue may be present.

The exposed cell cavity may be warty in appearance microscopically. This layer consists primarily of metabolic byproducts and residue from the protoplast.

The lignocellulosic cell wall may be further subdivided in four sublayers: S3, S2, S1, and P. (See Fig. 1.) The S layers are secondary wall layers differing primarily in orientation of cellulose microfibrils. The S3 is adjacent to the cell cavity. The S2 layer occupies the greatest volume of the secondary wall. The S1 layer is adjacent to the primary wall layer P, which lacks the fibrillar orientation of the secondary wall. The middle lamella consists primarily of lignin which bonds the individual fibers in wood.

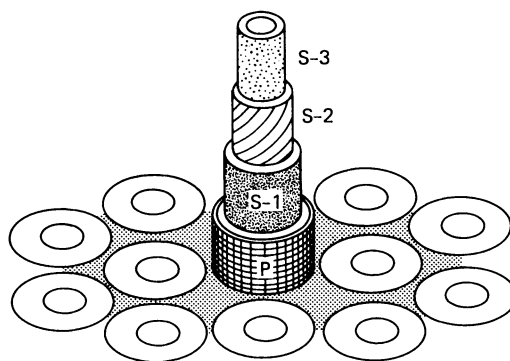


Fig. 1. Lignocellulose structure.

In addition to the major cell wall polymers already mentioned, extractives (low molecular weight organic molecules) may be present in differing amounts. While usually minor components (i.e., less than 5%), extractives may be present in quantities as high as 10–30% by weight in some species in the heartwood or in unhealthy wood. As cells die in the sapwood, extractives are deposited in those fibers, converting them to heartwood. The chemical composition of the extractives is variable, as is their influence on bonding. Water soluble sugars and tannins may migrate to the wood's surface during drying. Acidic extractives, frequently found in hardwood species, may interfere with proper wetting, act as a barrier to penetration of the adhesive, or interfere with resin cure resulting in bonding problems. Nonpolar extractives such as terpenes and fatty acids may also interfere with adhesive bonding. Although the cellular major and minor chemical constituents present a heterogeneous array of polarities and molecular sizes, wood-fiber surfaces are nonetheless readily bonded by many polar and nonpolar adhesives.

### The Influence of the Substrate's Physical and Chemical Structure on Bond Formation

Physical characteristics of the substrate having an influence on bond formation include wood anatomical features and wood physical properties. Chemical characteristics of the substrate

having an influence on bond formation are the wood's major components and minor components or extractives.

The cellular heterogeneity of wood results in surface roughness and variability in texture, porosity, density, and hardness or compressibility. Because of the rough surfaces, pressure is required to assure good wood-to-wood contact needed for bond formation. High density wood having a high hardness will be difficult to compress. Such woods are less conformable under pressure and difficult to bond. Adhesive penetrates more slowly in dense woods. The broad range of densities found in a single composite may create bonds of differing quality from region to region.

Wood is hygroscopic and may gain or lose water to the environment. When water is removed, the fiber wall collapses or shrinks. When the fiber wall absorbs water, it swells. Wood will equilibrate at constant temperature and humidity. But the environmental conditions of most composite manufacturing facilities are not constant. Wood is gaining or losing water and shrinking or swelling prior to, during the process of, and after bond formation. These dimensional changes influence the bonding process. Glueline stresses can develop during the curing process prior to the development of adequate cohesive strength. The shrinking and swelling of wood can also stress the glueline after the composite has been manufactured. Because of these possible stresses, wood is generally dried to a moisture content approximating that to be encountered during use.

Chemically, wood extractives may have the greatest influence on bond formation difficulties. They may reduce wettability. They may form a barrier at the interface causing mechanical weakness. Extractives can interfere with desired curing of the adhesive at the interface. This is of great concern if extractives alter the pH and buffer characteristics of the wood and the adhesive is sensitive to pH and buffer. External catalyst systems may be useful to overcome wood buffer problems.

The surface of the substrate can change chemically during heating and drying, resulting in thermal inactivation. Thermally inactivated wood surfaces may be less wettable and tend

to absorb less water from the adhesive. Possible causes are migration of extractives to the surface, pyrolysis, oxidation of hydroxyl groups or other chemical reactions of the surface.

## ADHESIVE SYSTEMS

A great variety of adhesives have been used as assembly glues with wood for home projects, furniture, and other nonstructural applications. Polyvinyl acetate (PVA) in aqueous emulsion is a common wood glue for such applications, but lacks water resistance and tends to creep under sustained load. Epoxy and urethane adhesives are costly, but are used in limited applications.

The greatest volume of wood adhesives for structural applications are thermosetting phenol-formaldehyde (PF) or urea-formaldehyde (UF) polymers or their derivatives. PFs are the commodity for exterior applications, while UFs are the commodity for interior applications. Because each composite product and the associated process may require a somewhat different resin, many variations of PF and UF resins are available. Isocyanate crosslinking resins are used to a lesser extent than PFs or UFs in manufactured board. Although these resins impart a durable, water resistant bond suitable for exterior application, the cost per pound of adhesive is greater than for PFs or UFs.

## Phenolic Resins

**General Properties.** Phenolic resins generally are aqueous solutions of alkaline-catalyzed phenol-formaldehyde polymers. A typical resin would be about 40% solids, containing phenol, formaldehyde, and sodium hydroxide in molar ratios of about 1:2:0.75, and might average 10–50 phenol units linked together. These can be spray dried for application as a dried powder. Phenol-formaldehyde resins are cured with heat under pressure. The resultant bond is highly water resistant and heat resistant. The durability and weatherability of phenolic-bonded wood composites enables them to be rated for exterior use.

Resorcinol is a derivative of phenol, having

an additional hydroxy group on the benzene ring. The hydroxy group is positioned such that it activates the molecule toward reaction with formaldehyde because the activity of the *ortho-para* positions is heightened. Partial substitution of phenol with resorcinol accelerates cure of these phenol-resorcinol-formaldehyde (PRF) resins. PRF resins or resorcinol-formaldehyde (RF) resins, in which all phenol had been replaced with resorcinol, may be used in applications such as lumber laminating where ambient-temperature curing is needed. These will cure without additional heat input. The bond is also waterproof and heat resistant and is rated for exterior applications. Phenol and resorcinol are the main phenolics used in phenolic resins, but a variety of other phenolic derivatives may be co-reacted in minor amounts to impart desired characteristics.

**General Chemistry.** Phenolic polymers are formed with a phenolic or phenol derivative monomer and formaldehyde crosslinking agent in two discrete steps. The first step, shown in Fig. 2, is an addition or methylation step. Formaldehyde reacts with an active *ortho* or *para* proton to form the addition product which

is a methylolated phenolic. Mono-, di- and trimethylol derivatives are possible.

The second step, shown in Fig. 2, is a condensation step. Water is generated as a condensation byproduct and is formed with a methylol hydroxy and neighboring active proton. The combination of addition-condensation steps yields a polymer network which is the backbone of the adhesive resin. The reaction steps leading to resin formation are generally performed at elevated temperature in a chemical reactor capable of heating, cooling, good agitation, vacuum distillation and atmospheric reflux.

The properties of the resin may be modified by varying any of the synthesis parameters. These variables include the molar ratio of formaldehyde to phenol, catalyst, their rate of addition, the concentration of raw materials during the cook, the type of catalyst used, the temperature profile during the cook, the presence of a dehydration step, the presence of a neutralization filtering step, the target nonvolatiles content, the degree of molecular advancement, and the presence of additives to impart special characteristics. The effect of varying the synthesis parameters is to vary the

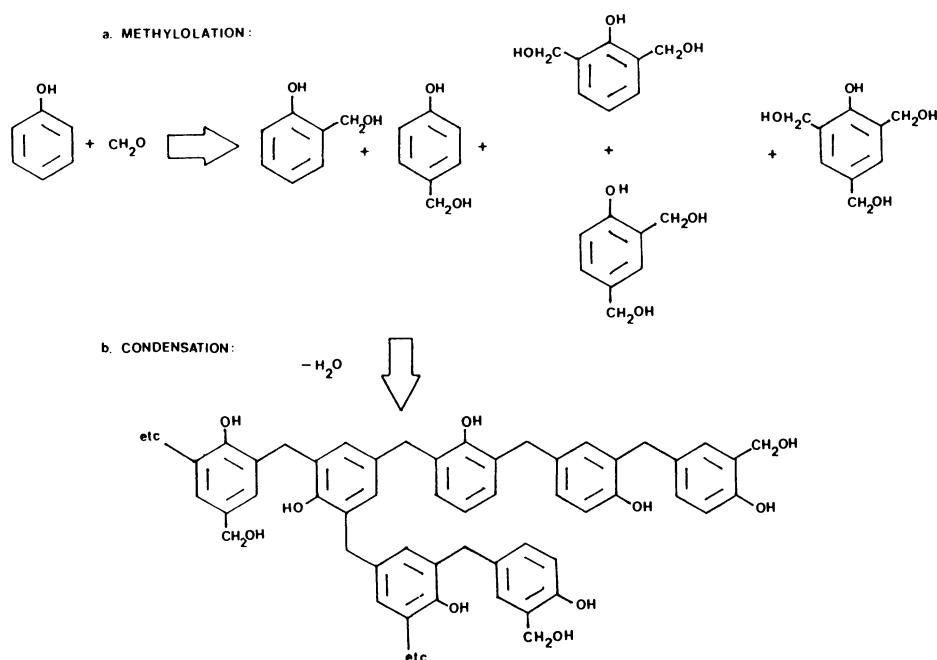


Fig. 2. Reactions in the formation of PF resins.

molecular and/or colligative properties of the polymer network. Properties monitored may include molecular weight, molecular weight distribution, functional groups, cure rheology, viscosity, and cure speed. By evaluating the molecular and colligative properties of the adhesive resin, its consistency may be monitored and its mill performance may be controlled.

**Applications.** PRFs and RFs are used primarily in lumber laminating and ambient temperature bonding applications. PFs are used primarily in hardboard, plywood, oriented strand board (OSB), and waferboard. It is used to a small extent in particleboard. Because PFs generally do not develop the tack of UFs, they are not easily used on caulless particleboard lines.

The resin may be applied as a neat liquid but more frequently is used in conjunction with extenders and fillers to improve gap filling, moisture retention, and cure characteristics and to control pot life. The resin may be spray dried and applied with molten wax or wax emulsion as a carrier. Products manufactured with phenolics are generally rated for exterior use.

## Amino Resins

**General Properties.** Amino resins are generally aqueous solutions of acid-catalyzed urea-formaldehyde (UF) polymers. A typical resin would be about 60% solids containing urea and formaldehyde in molar ratios of about 1:1.2. UFs are cured with heat under pressure and usually with an acid catalyst if the wood species is not acidic. The resultant bond is not water resistant, especially at elevated temperature. Formaldehyde is slowly released from UFs as they decompose. Even at low concentrations, the released formaldehyde may be a nuisance in poorly ventilated living quarters.

Melamine consists of a resonance-stabilized carbon-nitrogen six-membered heterocyclic ring with three functional amine groups. Melamine may be copolymerized with the urea in melamine-urea-formaldehyde (MUF) resin to increase the durability of the UF, but at an increased cost. Melamine may be used entirely

in place of the urea (MF), yielding a durable adhesive.

**General Chemistry.** UFs, MFs, and MUFs polymerize in discrete addition (methylation) steps and condensation steps (Fig. 3) similar to the chemistry previously described for PFs. There are four reactive sites on a urea molecule but only three sites may methylolate due to crowding.

Synthesis parameters are modified, as with the PFs, to alter resin properties. Molar ratio, catalyst system, raw material concentration and their rate of addition, target nonvolatiles, a dehydration step and additives may all be varied to modify and impart special properties to a resin. Properties monitored may include molecular weight, molecular weight distribution, functional groups, cure rheology, viscosity, and cure speed.

**Applications.** UFs are the primary commodity binder in caul and caulless particleboard processes and medium density fiberboard (MDF). They can be formulated to develop tack and generally are used as a neat liquid. Acid catalysts are frequently used unless the wood species is acidic such as southern pine or oak. Products manufactured with UFs are rated for interior application. Use of MUFs or MFs increases bond durability and imparts water resistance to the bond, speeds cure rate, and reduces potential formaldehyde release.

## Diisocyanates

**General Properties.** Diisocyanate resins are generally liquid, consisting of a mixture of lower molecular weight monomers and oligomers. The resin can be 100% nonvolatiles theoretically because no solvent is generated as a byproduct of the chemical reactions associated with cure. Isocyanates are very reactive and are cured with heat and pressure. The resultant bond is highly water resistant and heat resistant. The durability and weatherability of diisocyanate bonded wood composites enables them to be rated for exterior use. Diisocyanates can co-react with PF or UF resins, but are generally more expensive on a solids basis than either of the former.

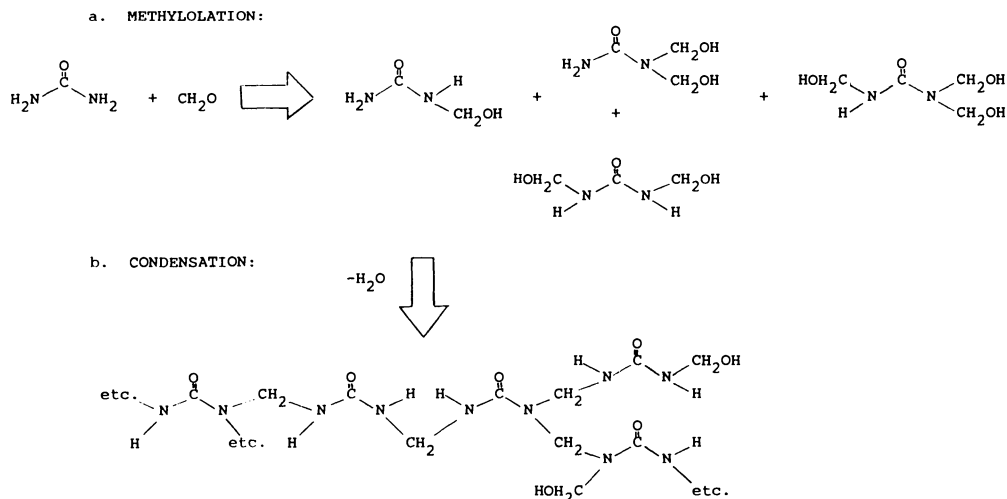


Fig. 3. Reactions in the formation of UF resins.

A typical diisocyanate resin is based on isomers of methylene-diphenyl-diisocyanate (MDI) as the monomer units. Other types of isocyanates can be used. Toluene-diisocyanate (TDI) is very reactive, but also very volatile. Because TDI is so volatile and reactive, it can crosslink in human lungs and it is therefore not practical for hot press applications in the wood industry. Because polymeric MDI (PMDI) has advantages of low vapor pressure, high reactivity, and acceptable viscosity, wood resins frequently consist of a significant percentage of PMDI (Fig. 4).

**General Chemistry.** The reactive portion of the isocyanate is the  $-\text{N}=\text{C}=\text{O}$  functional group. A stepwise addition reaction occurs across the double bond (Fig. 5). The  $-\text{N}=\text{C}=\text{O}$  group can react with active hydrogens under either alkaline or acidic conditions. A variety of self-reactions readily occur as well as reactions with water, alcohols, polyols, hy-

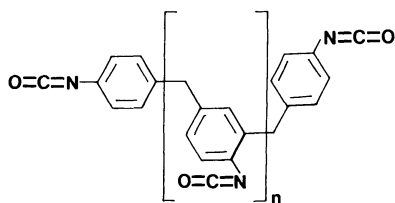
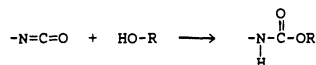


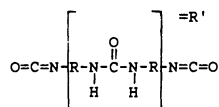
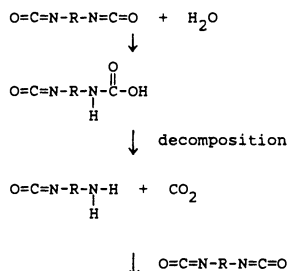
Fig. 4. Typical structure of polymeric methylene-diphenyl-diisocyanate (PMDI).

droxyls, and amines. Because too much water can deactivate the diisocyanates, wood moisture content must be carefully controlled. There

#### REACTION WITH HYDROXYL GROUPS:



#### CHAIN GROWTH WITH WATER:



#### POSSIBLE REACTION WITH WOOD HYDROXYLS:

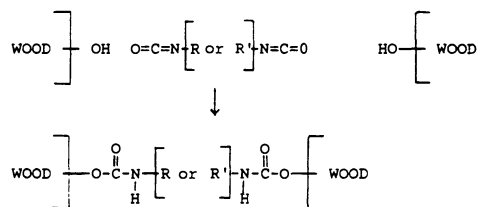


Fig. 5. Reactions in the formation of diisocyanate resins.

is a strong likelihood of covalent linkages between isocyanate resin and wood substrate. Because the  $\text{—N=C=O}$  group is also highly reactive with metals, release agents are frequently necessary to prevent permanent bonding to metal caul plates or press platens. Properties of the isocyanate resin may be modified by changing the monomers used in the resin or by reacting them with additives, such as polyols.

**Applications.** Isocyanates are used commercially to a minor extent in manufactured board as a specialty adhesive. They are used in particleboard, OSB, and waferboard for special products where color as well as exterior durability are important.

### **General Concepts of Adhesive Structure–Property Relationships**

Resin chemistry is a mixture of thermodynamic and kinetic knowledge, semiempirical theory, and formulation art. Chemists have sought and continue to seek instrumental and other methods to predict performance prior to plant trials. Methods of chemical analysis, rheological characterization, mechanical analysis, pilot plant evaluation, fracture mechanics, and multivariate statistical analysis all are useful tools. Lab studies are generally designed to bracket the conditions which are likely to be encountered in field trials. When trends are identified, theoretical explanations are formulated.

The performance properties of a resin may then be predicted based on structural data which chemically or otherwise characterizes the resin. Because data frequently are generated in a lab or pilot experiment, field trials are necessary to confirm the theory generated by the trend analysis. Generally, the same trend will be identified in the field trial if the lab experiments were properly designed. The magnitude of the trend, however, is likely to differ between controlled lab or pilot experiments and daily mill operation. Formulation changes are then needed to accommodate mill operating and environmental peculiarities. The observational skills of the formulation chemist are the art in these manipulations of the resin formulation. Because of mill operating and environmental peculiarities,

resin chemistry likely will remain for many years as a mixture of thermodynamic and kinetic knowledge, semiempirical theory, and formulation art.

### **VENEER AND SOLID WOOD COMPOSITE PRODUCTS**

Veneer and solid wood composite products are manufactured for building and construction commodity markets and for specialty markets such as marine applications and aesthetic decor. Bonding systems vary based upon the service demands placed upon the final product, interior versus exterior. Construction and decorative plywood are veneered panel products. Laminated veneer lumber (LVL) is a veneer product which competes with lumber. Lumber laminates form majestic beams often for dual structural and aesthetic applications.

Construction plywood is primarily phenolic bonded for an exterior rating. Decorative plywood is primarily bonded with UF resins for interior applications such as wall panels and hardwood flooring tiles. Both types of plywood are composed of layers of veneer or wood with alternating grain orientations that are bonded with heat and pressure.

As the thickness of the wood members to be bonded increases, heat transfer from the hot press becomes limiting, and a more reactive resin system is required. Radio frequency (RF) curing processes may also be used. Laminated veneer lumber may be heat cured if the composite thickness allows heat transfer. Alternately, PRF resin systems are used which will cure at ambient temperature. PRF resin systems are used in lumber laminating applications and are cured at ambient temperature under pressure, generally with a catalyst to promote cure.

Adhesive systems for construction plywood, decorative plywood, LVL (laminated veneer lumber), and lumber laminates are a heterogeneous mixture consisting primarily of resin with extenders, fillers, and catalysts. The adhesive mixture allows for a better matching of adhesive with mill operating parameters than would easily be obtained solely with the use of neat resin.

The blending of a resin with other ingredi-

ents frequently results in reduced overall glue costs. But cost is only one of several benefits gained by using an adhesive mix. Extenders, such as wheat flours, are used to manipulate the hygroscopicity of the adhesive mix. Manipulation of the adhesive's hygroscopicity allows control of the glue's tendency to dry out at one extreme or overpenetrate due to excessive moisture at the other extreme. These tendencies must be controlled by mill operators to respond to changing mill conditions, such as wood species mix and ambient temperature and relative humidity, which influence the wood's equilibrium moisture content.

Fillers, such as nutshell flours, remain partially undigested in an adhesive mix. These tend to reinforce the physical strength of the glue-line when properly cured. When glue-line stresses such as expansion and contraction initiate a fracture in the glue-line, the fracture tends to propagate. The fracture propagates because the stresses become concentrated at the crack tip and because thermosetting crosslinked resins tend to be brittle when cured. When a propagating crack tip contacts a filler particle, the stresses are then redistributed over a greater volume of material, which effectively stops the propagation of the crack and disperses the stresses in the vicinity of the crack tip.

The glue-line in a veneer product is generally thought of as a continuous film. The surface of the veneer is frequently rough and imperfect, containing lathe checks. The core layers of veneer products may contain additional voids due to knots and gaps between edge-butt joint veneer. An additional benefit of incorporating the resin into an adhesive mix is the ability of the mix to aid in gap-filling and bulking of the adhesive between veneers. Catalysts may also be added to the mix to regulate cure speed. The pot life of the adhesive must be monitored in all gluing applications.

## MANUFACTURED BOARD

In contrast to veneer composites, in which the glue-line is present as a continuous film, in manufactured board products the bonding sites are present as spot welds. The wood particles range in size from fibers in hardboard and fiberboard, to a mixture of fibers and particles in

particleboard, to long thin particles or strands in oriented strand board, to thin wafers in waferboard. PF resins are primarily used in hardboard, oriented strand board, and waferboard. UF resins are primarily used in fiberboard and particleboard, although some PF and isocyanate resins are used to a limited extent in some particleboard applications.

*Hardboard* is manufactured either by a wet process or a dry process. Either thermomechanical or mechanical milling may be used to reduce the wood chips to fibers or pulp. A water suspension of fibers is formed on a moving screen which is hot pressed to a high density board in the wet process. Resin (usually 1–2% PF solids on a wood solids basis), wax, retention aids, and wet strength additives may be added to the slurry. Exterior home siding is one of many markets for this product. Alternatively, the mat may be formed with dried fiber that has already been blended with resin, then pressed for dry process hardboard. Low density insulation board also may be manufactured from fibers with wax and little or no additional binder. Board properties may be modified by adjustment of pulp additives in the wet process, bond forming parameters, press closing rate, press temperature, press time, and post-press coatings.

Fibers used in the manufacture of *medium density fiberboard* (MDF) do not go into a slurry mix. The wood chips are generally fed into a pressurized steam injected digester which thermally softens the chips. Upon release from the digester the chips pass from high pressure to low pressure and are passed through a rotating disk refiner. The combination of depressurization and refining forms a thermomechanical pulp. The fibers go directly to dryers after refining. UF resin and wax may be applied at the point between refiner and dryer in *blow line blending*. The resin does not advance appreciably in the dryer. Alternatively, the resin may be applied by a conventional blender after the fibers are dried. The blended fibers are formed into a mat and hot-pressed. An RF unit may be used to assist in resin cure. Because of the generally tight edges and smooth surface of MDF, great quantities are consumed by the furniture industry. The tight edges are good for cutting edge profiles while the smooth surfaces provide



a good substrate for vinyl print or paper overlays.

*Particleboard* is manufactured from wood chips or shavings from lumber planing mills which are mechanically reduced to particle size (0.5–3 mm wide by 1–30 mm long). Management of wood shavings inventory, the milling and the drying of shavings control the quality of particles used in board manufacture. Bulk density and particle geometry influence the mat handling characteristics on the production line and the final obtainable board physical properties. Finer particles are segregated either mechanically or air classified by blowing air and deposited in surface layers during mat formation, while coarser particles go into the core or center of the board. In the blending and forming operation, the surface and core furnish may be handled separately and may even use different resin systems. In addition to all of the previous operations, moisture content, wood species mix, press closing and decompression rates, and press cycles all influence the board's final physical properties obtained. For floor underlayment applications, modulus of rupture is an important physical property. The market pays a premium for industrial particleboard that can be used as furniture components. Particleboard is becoming more competitive with MDF by producing smoother surfaces and tighter cores. Because particleboard and MDF are generally used for interior applications, they are bonded with UF resins. MUF, PF, and isocyanate resins are used where additional durability or reduced formaldehyde emissions are critical.

The wood chips for *oriented strand board* (OSB) are milled so that they are dimensionally larger in the longitudinal direction (i.e., 2–10 cm) and narrow in the radial direction (i.e., 0.1–2 cm). Because wood is anisotropic, the strands are layered with the core strands perpendicular to the surface strands, similar to the layers of veneers in plywood. The resulting board has good dimensional stability. OSB competes with plywood for sheathing and siding applications and is bonded with PFs or isocyanates for exterior durability.

The wood chips for *waferboard* are milled into flakes or wafers (i.e., 1–4 cm wide by 3–8 cm long). They are bonded with either a liq-

uid PF resin or a spray dried, powder PF resin which is distributed onto the individual flakes with the assistance of molten wax or wax emulsion which also acts as a sizing agent. Waferboard is used for sheathing and siding.

## FUTURE CHALLENGES

Some future challenges can be predicted already based on current trends, driven either by the marketplace or by government regulators, which may be extrapolated into the future. Market driven challenges are generally motivated by a desire to increase profitability or to improve quality (which results in improved profitability). The changing availability of adhesive raw materials can alter the relative price structure of resin systems. Government regulations can alter the availability of resin systems or the potential liability of working with a given adhesive system.

Dryer capacity is a limiting factor in many plywood manufacturing plants and a source of high energy costs in most board-making operations. The ability to bond veneers and particles at a higher moisture content represents a potential cost savings and increased productivity in plywood and board manufacture. A current and future market driven trend is to develop adhesive systems which will cure when used to bond wood at a higher moisture content.

The upgrading of particleboard for industrial applications is a challenge directed at improving product quality. The majority of opportunities for improving board quality are in mill operating parameters. Opportunities for modification of the resin system for improved surfaces lie in going from single resin systems to surface and core resin systems. The incorporation of melamine into the resin system may further enhance board surfaces, but at higher resin cost.

The supply of raw materials for adhesives is closely tied to the availability of petroleum. Toluene and other raw materials for the synthesis of phenol are also used as octane boosters for unleaded gasoline. Availability and price are often volatile. Adhesive manufacturers are challenged by opportunities to use alternate raw materials. Board manufacturers are challenged by variable adhesive costs. Naturally occurring

phenolics derived as byproducts of wood utilization have found a use in resin systems in many parts of the world, but have not yet been economical in the U.S. However, those economics are subject to change based on the availability of petroleum.

Government regulations have historically focused on formaldehyde emissions from manufactured board products. These emissions are primarily associated with UF resin systems. Modern UF resin formulations have drastically reduced emissions. Board surface porosity can also be decreased to reduce emissions. Even with improvements in board surfaces and UF resin systems, the specter of additional regulation cannot be overlooked.

Isocyanate resins, although expensive, were once viewed as a possible alternative to UF resins. Isocyanates are highly reactive and pose certain health hazards during board manufacture, particularly fumes near the hotpress. The mill workers' health may be a future concern to regulatory agencies.

Opportunities to meet future challenges are limited only by the creativity of the industry. Products exist in the marketplace now which were merely concepts five years ago, and were unrecognized as opportunities ten years ago.

Ten years into the future may see new board products, new bonding applications, and new innovative adhesive systems. Some future challenges can be predicted based on current trends and will be met by those who currently see opportunities to meet those challenges. Some future challenges cannot be predicted. By extrapolating the individual and collective industrial ability to formulate opportunities to meet past challenges, the unpredictable future challenges will also be met with creative, effective and profitable solutions which will benefit our society.

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## Sealants and Caulks

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Sealants and caulks are used to fill joints, gaps and cavities between two or more similar or dissimilar substrates. Sealants and caulks seal these discontinuities in structures for economy, convenience, and functional necessity. Their purpose is to isolate and control conditions, such as water and weather, to optimize the functioning of the structure being sealed. Today the number of applications for sealants and caulks in construction, industrial and consumer markets is growing. These materials are required to seal and adhere to the appropriate mating surfaces over a wide range of temperatures, environmental stress and joint movement conditions. These surfaces to be sealed include a wide variety of glass, concrete, masonry, wood, steel, aluminum, and plastic substrates.<sup>1-11, 87, 98, 102</sup>

*Caulks* are materials used for sealing substrates where only minor or no elastomeric properties are required. *Sealants* are elastomeric materials with adhesive qualities used for sealing substrates. *Sealant/adhesives* are elastomeric materials with adhesive qualities which provide structural strength when joining substrates. These materials range from noncuring mastics to curable elastomeric sealants, and

from noncuring tapes to extruded preformed tapes; types of materials vary from bituminous to high modulus silicone polymers. For purposes of this discussion, sealants and caulks will be classified as low, medium, and high movement products.<sup>98</sup>

Over the last 40 years, a wider variety of sealants and caulks, especially high performance sealants, have been developed to satisfy the new high technology needs of transportation, aerospace, and construction applications (see Fig. 1). An example of the increased sealant performance requirements was the introduction of curtainwall construction in the early 1950s as a new architectural design. It created the need for sealants that compensate for foundation settling, temperature changes and wind-created stresses on the curtainwall panels. The cured sealant must demonstrate adhesion and movement capability while resisting the deleterious effects of temperature extremes, water, sunlight, and environmental pollutants.<sup>80</sup>

The sealant must absorb stresses when the curtainwall panels shift relative to each other because of the settling of these high-rise building with live and dead building loads. These stresses on the sealant are shear, compression,

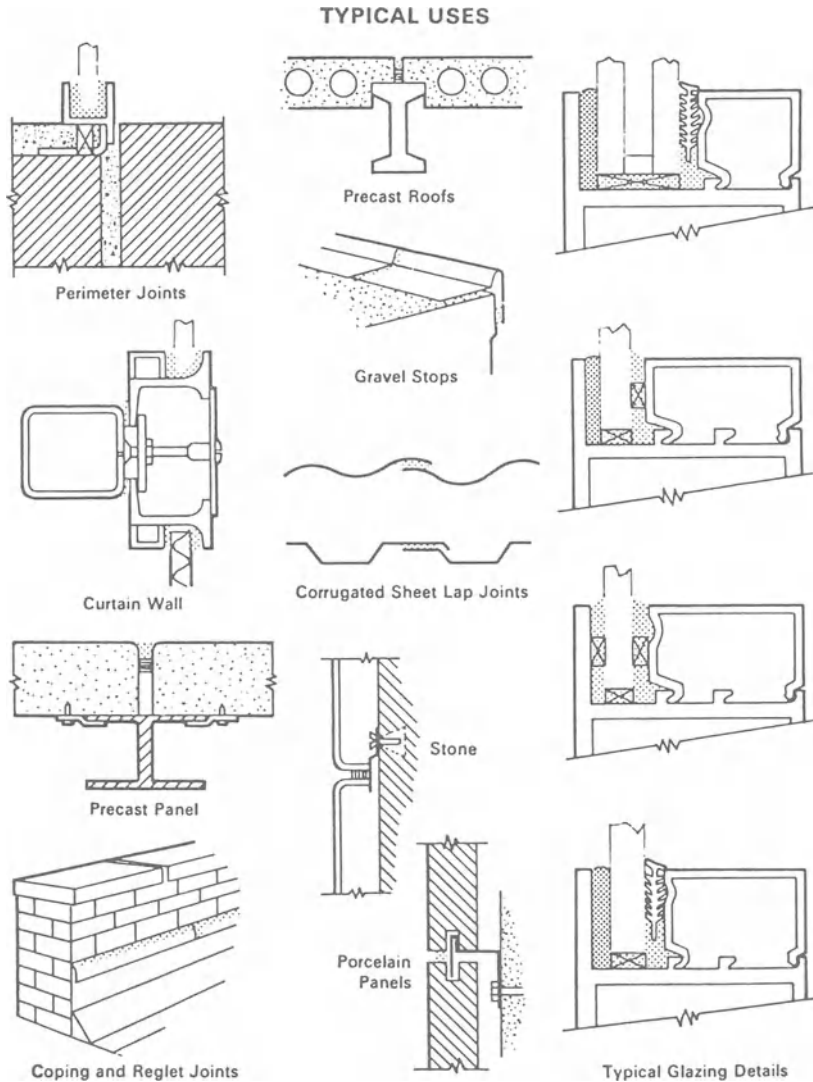


Fig. 1. Construction applications for sealants.

and extension. The sealant must compensate for thermal expansion and contraction of a wide variety of curtainwall materials. Table 1 lists the coefficient of thermal expansion of a variety of substrates. The sealant must seal common curtainwall materials such as aluminum and glass, with aluminum having a thermal coefficient of expansion 2.5 times that of glass. The sealant must compensate for the stresses caused by wind loading, which will place both positive and negative loads on the curtainwall system. The sealant will have to accept a skewed squeezing and pulling effect due to the curtain-

wall panels' wind-created bending and flexing. For example, an  $8' \times 10' \times \frac{3}{8}"$  thick lite of plate glass will deflect  $1\frac{1}{8}$  inches at its center under a 120 mph windload. With all these stresses, the sealant must maintain a watertight and airtight structure in these curtainwall designs over time in a wide range of environmental conditions. Furthermore, these sealants must maintain their movement capability and adhesion with acceptable aesthetics.<sup>102</sup>

This chapter will overview the types of caulks and sealants available today. Typical formulations and properties will be presented for the

**Table 1. Coefficients of Linear Expansion of Common Building Materials (in./in.-°F × 10<sup>-6</sup>).**

Clay, masonry (Brick, clay or shale)	
Brick, fire clay	3.6
Tile, clay or shale	3.3
Tile, fire clay	2.5
Concrete	
Gravel aggregate	6.0
Lightweight structural	4.5
Concrete, masonry	
Cinder aggregate	3.1
Dense aggregate	5.2
Expanded-shale aggregate	4.3
Expanded-slag aggregate	4.6
Volcanic pumice & aggregate	4.1
Metals	
Aluminum	13.0
Brass, red 230	10.4
Bronze, arch. 385	11.6
Copper, 110	9.8
Iron	
Cast gray	5.9
Wrought	7.4
Lead, common	16.3
Monel	7.8
Stainless steel	
Type 302	9.6
Type 304	9.6
Structural steel	6.7
Zinc	19.3
Glass, plate	5.1
Plaster	
Gypsum aggregate	7.6
Perlite	5.2
Vermiculite aggregate	5.9
Plastics	
Acrylics	40-50
Lexan®	37.5
Phenolics	25-66
Plexiglas®	39
Polyesters, glass reinforced	10-14
PVC	33
Vinyls	24-40
Stone	
Granite	6.2
Limestone	3.5
Marble	7.3

various polymer types, as well as information on how to select, test, and properly install sealants and caulks.

## FORM, TYPE, AND PERFORMANCE

### Forms

**Tubes or Cartridges.** These are filled caulking cartridges, typically 10.7 ounces to one quart, applied by hand or power-activated caulking guns.

**Bulk Materials.** These are single or multi-component sealants and caulks sold in units from 1.5 to 50 gallons, to be applied by knife or filled into caulking cartridges (see Fig. 2) or mechanical pumping equipment. Multicomponent materials (two or more components) are typically mixed by powered drill mixer (see Fig. 3) or meter mix equipment.

**Extruded Tapes.** These are preformed ribbons or profiles of butyl rubber, neoprene, or polyvinyl chloride, and may be either solid or expanded. They may be supplied as composite structures with rubber cores, rubber rod spacer, or aluminum shims surrounded or embedded in an adhesive or sealant.

### Types

As supplied in a cartridge, in bulk or as extruded tapes, sealants and caulks are of nine types, described below.

**Hot Pour Sealants.** These must be melted to the recommended temperature for proper handling and performance (especially adhe-



Fig. 2. Sealant application from caulking cartridge.



Fig. 3. Power mixing.

sion). Application should be in one operation, and remelting is not advised unless permitted by the manufacturer.

**Cold Pour, Multicomponent, Chemically Cured Sealants.** These materials cure by chemical reactions, usually involving the crosslinking of polymers. The sealant base, curing agent, and color pack (if required) must be thoroughly and uniformly blended. It is essential that the full contents of the curing agent be transferred to the base prior to mixing according to the sealant manufacturer's specifications. These materials can be poured directly from the mixing vessel into the joints to be sealed.

**Nonsag, Noncured Sealants.** These non-curing materials are sufficiently thixotropic to be applied in vertical joints without appreciable sag or weep. They are applied with a knife or caulking cartridge into the joint and forced against the sides of the substrates. They may require warming to be applied properly.

**Nonsag, One-Part, Chemically Cured Sealants.** These materials cure by chemical reactions, usually involving the crosslinking of polymers. They are applied by knife, caulking cartridge, or bulk dispensing equipment into the joint, being sure to wet out the sides of the substrates. Manufacturer's recommendations should be followed for types of bulk loading guns, nozzles, and bulk dispensing equipment.

**Nonsag, Multicomponent, Chemically Cured Sealants.** These sealants also cure by chemical reactions, usually involving the formation of crosslinked polymers. The sealant base, curing agent, and color pack (if required) are mixed together according to the sealant manufacturer's recommendations. After mixing, the sealant is filled into cartridges, dispensed from automatic mixing equipment, or applied with a knife.

**Heat-Softened, Nonsag Sealants.** These sealants and caulks require heating to be properly dispensed and applied. They may be heated in ovens, heat chests, or boiling water to the manufacturer's recommended temperatures. For proper application and performance, care must be taken not to overheat them prior to application, nor to apply below the manufacturer's minimum temperature recommendations.

**Strip Sealants—Cold-Applied Mastic Strips.** These sealants are supplied with backing paper for proper handling and application. A suitable length of the strip sealant is applied (adhered) to one of the joining surfaces with backing still in place. The paper is then removed and the other joining surface is placed in position for sealing. Exact storage, handling, and application instructions must be followed.

**Strip Sealants—Hot-Applied Preformed Strips.** These sealants are also supplied with backing paper. The backing paper is removed from a suitable length of strip sealant and fit into the slot to be sealed. The strip is then heated to the manufacturer's recommended temperature. Caution must be taken that the heat-softened material achieves continuous

contact with the sides of the joining surfaces to be sealed.

**Compression Seals.** These are preformed cellular elastomeric products available in either precompressed or uncompressed forms. The sealant may utilize external and/or internal adhesive elements. The seal is obtained by placing the preformed material in compression between the joining surfaces. Exact storage, handling, and application instructions must be followed.

### Performance

Sealants and caulks fall into three categories: low, medium, and high movement materials. They vary widely in the test properties shown in Table 2.<sup>98</sup>

**Table 2. Sealant and Caulk Properties.**

<i>Property</i>	<i>Typical Units</i>
<b>Uncured</b>	
1. Skin-over time	minutes
2. Tack-free time	hours
3. Sag, weep	inches
4. Extrusion rate	grams/minute
5. Flow	seconds
<b>Cured</b>	
1. Durometer hardness	Shore A points
2. Tensile at maximum elongation	pounds/inch <sup>2</sup> percent
3. Elongation at maximum tensile	pounds/inch <sup>2</sup> pounds/linear inch
4. Modulus	pounds/linear inch
5. Tear	
6. Peel	
<b>Application</b>	
1. UV resistance	
2. Ozone resistance	
3. Staining/dirt pickup	
4. Color change	
5. Application temperature range	
6. Service temperature range	
7. Adhesion	
8. Durability	
9. Compatibility	
10. Compression set	
11. Solvent resistance	
12. Life expectancy	
<b>Cost</b>	
1. Material	
2. Installation	

The key performance properties most often used to select a sealant or caulk are movement capability, adhesion, life expectancy, and material cost. With the proper design and assembly of the structure to be sealed, a critical property is the amount of movement a sealant or caulk will accept prior to failure, expressed in percent extension (+) and percent compression (−). Adhesion is the tendency of a sealant or caulk to bond to a surface or material when under a separating stress. Sealants can fail in adhesion by cleanly separating from the surface (adhesive failure) or tear internally in the sealant, not affecting the bond line between the sealant and surface (cohesive failure). Sealants and caulks will vary in their performance longevity with regard to weathering, temperature and chemical environment of the application. Always a consideration is overall cost, which embraces material cost, installation cost, and life cycle cost (performance and life expectancy). Table 3 outlines a range of caulks and sealants and their characteristics.<sup>6,10,98</sup>

### POLYMERS FOR SEALANTS, CAULKS, AND GLAZING COMPOUNDS

Sealants, caulks, and glazing compounds are normally highly pigmented (40–80%) compositions based on a wide variety of polymeric vehicles. Some 15 families of polymers are utilized singly or in polyblends to achieve the storage characteristics, application properties, physical performance, and durability required for each application at minimum cost. They are discussed here in order of increasing cost.

#### Asphaltic and Other Bituminous Materials

Asphaltic materials are supplied in solvent-diluted, emulsion, or hot-poured forms. Rubber is used for reinforcement in high solids formulations. The latter are more important because of better adhesion and lower shrinkage. Typically, the sealant contains 50–60% asphalt blend (needle penetration 10–110), 20–30% ground rubber (from tire scrap) and 20% cyclic hydrocarbon. The sealant is applied at 250–400°F. Durability can be as high as 5 years if properly applied.

**Table 3. Sealant Characteristics.**

	<i>Movement Capacity</i>	<i>Advantages</i>	<i>Disadvantages</i>
<b>Lower Movement Caulks</b>			
Oil/resin-based	±5%	Lowest cost; easily applied and tooled; primerless preparation; good color stability; fast skinning	No recovery; slow curing; can stain substrate; moderate shrinkage; for static joints
Polybutene/polyisobutylene	±5%	Good adhesion; low shrinkage; excellent UV/ozone resistance; low cost; good water resistance	Dirt pickup; low cohesive strength; poor solvent resistance; can stain substrate; for static joints
<b>Medium Movement Caulks and Sealants</b>			
Latex	±7.5%	Fast skinning and cure; immediate paint-over; good adhesion/UV resistance; easy application/cleaning	High shrinkage; poor water resistance; can freeze below 0°F; mostly indoor use
Butyl	±7.5%	Good adhesion; good water resistance; good color stability; little surface preparation; caps neoprene gaskets	Slow curing; high shrinkage; low recovery; relatively soft
Hypalon	±12%	Excellent UV/ozone resistance; impervious to water; fair recovery; remains flexible	Slow curing; high cost; high shrinkage; tough gunnability; not for interior use
Neoprene	±12%	Bitumen/asphalt compatible; good water resistance; good adhesion to metals; low cost	High shrinkage; only dark color; very slow curing; stains wood/stone
Solvent Acrylic	-7.5% to +12%	No primer required; excellent adhesion; excellent UV resistance; good chemical resistance; nonstaining; tough curing	$\frac{3}{4}$ " maximum width; poor recovery; strong curing odor; poor water resistance; slow curing
<b>Higher Movement Sealants</b>			
Polysulfides	±25%	Good UV/water resistance; won't stain masonry; fast through cure; good adhesion/durability; broad color range	Slight curing odor; less UV resistance/recovery than the following; primer required for porous surfaces
Urethanes	±25%	Excellent UV/ozone/tear/chemical resistance; excellent recovery; little shrinkage; joints up to 6" wide; 20-30 year life	Light colors can discolor; poor water immersion resistance; surface priming required
Silicones	±25% to ±50%	Excellent UV/ozone/heat resistance; no shrinkage; 20-30 year life; excellent recovery; nonstaining	Surface preparation critical; slight curing odor; dirt pickup; concrete/aluminum adhesion difficult



## Oleoresinous

Vegetable oils are used as the binder for putties, elastic glazing compounds, and architectural caulking compounds.

**Putties.** Used in the glazing of wood sash, putties are generally based on linseed oil, filled with calcium carbonate or blends of calcium carbonate and titanium dioxide. Formulations are shown in Table 4. Containing 11–12% oil, they dry by oxidation to hard, inflexible joints with little movement possible. Putties are supplied as bulk compounds for knife application to wood or metal sash. Most putties are used in industrial, commercial, and maintenance glazing; however, significant quantities continue to be used by homeowners in residential glazing.<sup>102</sup>

**Elastic Glazing Compounds.** Based on blown soya or linseed oils, these materials are formulated with selected calcium carbonates and fibrous fillers plus small amounts of fatty acids for easy working properties (knifing) on large glazing installations. Most of these materials are used in industrial and commercial construction and maintenance.

**Architectural Caulking Compounds.** These materials, also called oil-based caulking compounds, contain 15–20% blown or heat-bodied vegetable oil, usually soya, plus 5–8% fatty acids and polybutenes. Since these latter polymers do not harden on aging, they prevent embrittlement of the compound. Pigmentation is usually high in calcium carbonate, with fibrous talc or other fibrous filler to provide non-slump characteristics. Solvents up to 3–4% are often added to improve working. Oil-based

**Table 5. Elastic Glazing Compound (Professional Glaze).**

	% weight
Clarified raw soybean oil	7.0
Aged linseed oil (blown)	2.0
Soya fatty acids	0.2
Mineral spirits	1.8
Calcium carbonate, fine	30.0
Calcium carbonate, coarse	55.5
Fibrous talc	3.5
Total	100.0
lb/gal	18.6
Nonvolatile, %	98

caulks are lower in viscosity than glazing compounds, consequently can be applied from caulking cartridges rather than by knife.<sup>102</sup>

## Polybutene

The C<sub>4</sub> olefins go into three types of sealants: polybutenes, butyl rubber, and polyisobutylene. Polybutenes are largely linear, low molecular weight homopolymers of butene-1, used in sealants either as prime vehicles or as modifying polymers. They are relatively low cost, nondrying, tacky polymers. They are used in the formulation of three types of compounds:

1. *Nondrying mastic sealers* for concealed metal-to-metal joints where elasticity and resistance to staining are not essential, e.g., hidden joints in curtainwall construction, acoustical sealants, hidden automotive panel sealants, and gap fillers.
2. *Rope caulks and extruded tapes* for non-critical glazing and weatherstripping ap-

**Table 6. Architectural Caulking Compound (Drying Oil Caulk, Gun Grade, Neutral Shade).**

	lb	gal
Blown soybean oil	245	30.0
Polybutene (920–950 MW)	110	15.0
Soya fatty acids	16	2.0
Calcium carbonate, fine	800	35.6
Fibrous talc	200	8.4
6% Cobalt naphthenate	4	0.5
Mineral spirits	55	8.5
Total	1,430	100.0
lb/gal	14.3	
Nonvolatile, %	96	

**Table 4. Linseed Oil Putties<sup>a</sup>**

	Type I, % weight	Type II, % weight
Calcium carbonate (max.)	88	79
TiO <sub>2</sub>	—	10
Linseed oil (min.)	12	11
Total	100	100
lb/gal	18.3	19.6
Nonvolatile, %	99+	99+

<sup>a</sup>Federal Spec. TT-P-791a, modified: white lead replaced by TiO<sub>2</sub>.

**Table 7. Polybutene-Based Sealant (Rope Caulk).**

	% weight
Polybutene (1300–1500 MW)	27.4
Petrolatum	3.2
Tall oil fatty acid	0.6
Fibrous talc	34.4
Calcium carbonate	32.6
Titanium dioxide (rutile)	1.8
Total	100.0
lb/gal	13.8
Nonvolatile, %	99+

plications or for bedding compounds in small window frames. (Table 7 illustrates a typical rope caulk.) A knife-applied mastic sealer would have about the same percentage of a lower molecular weight polybutene. Rope caulks and polybutene tapes are sold in rolls of up to 100 feet.

3. *Plasticizing modifiers* for oleoresinous caulks, butyl caulks and tapes, and for certain elastomeric sealants.

### Butyl Rubber and Polyisobutylene

Polyisobutylene, PIB, is a homopolymer of high molecular weight. The butyl elastomers are copolymers of isobutylene with sufficient isoprene (0.5–2.5%) to permit crosslinking. Most butyl compositions are one-component, e.g., tapes or liquid gun-grade caulks. They may be modified with plasticizers such as polybutene, or tackifiers and fillers such as calcium carbonate and fibrous talc. Two-component, curing butyl sealants are also available.<sup>12,13,19</sup>

Premasticated butyl cutbacks for the sealant industry are also available, as are a series of depolymerized butyls, to improve compounding and processing ease. Chlorobutyl rubbers are also produced; these have found limited use in sealant formulations, mostly in tapes.

### One-Component Butyl Caulks.<sup>12,13</sup>

These are superior to oleoresinous caulks in weather resistance, ozone resistance, and impermeability to gases and vapors. Although not truly elastomeric, they can be used safely in joints with movement of up to 10–15%. They are solvent solutions of uncured butyl elastomers with 17–20% polymer and solids content

of about 75–85% NV. They shrink significantly; nevertheless, they can be formulated with fillers and plasticizers to increase their solids level. A low percentage of a drying oil, e.g., 3% dehydrated castor oil, encourages skinning and resistance to dirt pickup. These caulks are applied by gun. A typical composition is shown in Table 8.

**Two-Component Sealants.<sup>14–17</sup>** Two-component butyl sealants are room temperature vulcanized materials. Low in moisture vapor transmission and easy working because of low molecular weight and semi-liquid form, these sealants are filled with calcium carbonate and titanium dioxide, plasticized with polybutene, and may be modified with epoxy and silane adhesion promoters. The cure system is *p*-quinone dioxime activated with a peroxide.

**Preformed Tapes.<sup>18–20</sup>** Preformed tapes of butyl, usually vulcanized, are extruded semi-solid sections with pressure-sensitive adhesion. Since they are 100% solid, there are no problems of shrinkage or solvent evaporation. Sold in rolls interlined with release paper, they are often used together with liquid sealants or solid spacers, shims, etc. They vary from low cost, highly polybutene-extended tapes for trailers and mobile homes, to partially or fully vulcanized butyl rubbers with little polybutene content for high-rise glazing and automotive windshield sealants.

**Table 8. Butyl Caulking Compound (Gun Grade, Aluminum Shade).**

	lb	gal
Butyl rubber (035 grade, 50% NV in mineral spirits)	388	55.0
Petroleum resin (60% NV in mineral spirits)	74	10.0
Hydrogenated rosin, methyl ester	8.5	1.0
Denatured ethyl alcohol	1.3	0.2
Amine-modified bentonite	25	1.7
Calcium carbonate, fine	400	17.8
Fibrous talc	100	4.2
Aluminum paste (73.5% NV in mineral spirits)	34	2.5
Mineral spirits	50	7.6
Total	1,080.8	100.0
lb/gal	11	
Nonvolatile, %	74	

**Table 9. Butyl Rubber Architectural Sealing Tape (Light Gray).**

	<i>lb</i>	<i>% weight</i>
Butyl rubber (268 grade)	100	21.2
Calcium carbonate, surface coated	200	42.4
Silica, hydrated, precipitated	50	10.6
Zinc oxide, surface treated	10	2.1
Antioxidant, phenolic type	2	0.4
Polybutene (1300 MW)	100	23.3
Carbon black, furnace type, FEF	<u>0.1</u>	<u>0.02</u>
Total	472.1	100.0
lb/gal	13	
Nonvolatile, %	99	

A typical intermediate performance butyl tape contains 20–22% uncured butyl polymer, 20–25% high molecular weight polybutene, and pigmentation from calcium carbonate or silica, plus zinc oxide or phenolic antioxidants.

Partial crosslinking is achieved in the intensive mixing operation in the presence of high surface area fillers. This vulcanization increases tape strength and elasticity, and reduces compression set.

High performance elastomeric butyl tapes are available for large window lite glazing in high-rise structures and for windshield sealing. These usually contain crosslinked butyl elastomers (20–40%) plus polybutenes, resinous tackifiers, and reinforcing fillers such as carbon black and platy talc. Chlorobutyl rubber compositions are available for faster and more thorough vulcanization.

**Hot Melt, Field-Extruded Sealants.** Several butyl raw material manufacturers and sealant producers have recently developed butyl tapes. These are premasticated, high viscosity thermoplastic compositions that are fed as talced ribbons into a polymeric sealant applicator (PSA). Within the PSA, the compound is heated and extruded into the joint opening to form a smooth joint that cools rapidly with excellent adhesion claimed, even to oily or otherwise poorly prepared surfaces. These hot-applied, post-formed butyl tapes have been successfully used to seal insulated glass units, automotive windshields (Fig. 4), curtain walls, concrete pipes, precast concrete structural joints, and as bedding compounds in combi-

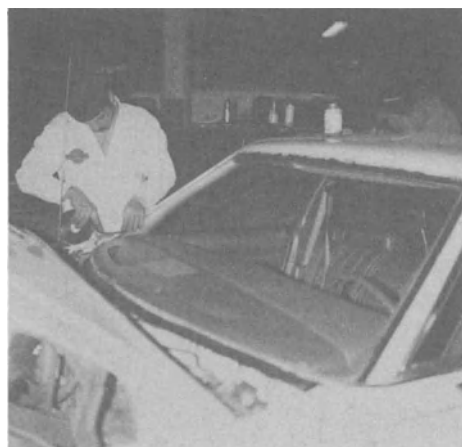


Fig. 4.

nation glazing.<sup>22–26, 86, 91</sup> Figure 5 shows the application of a patented extruded tape to an insulated glass unit in which the spacer and desiccant is incorporated into the sealant. This patented product combines these three components, typically applied separately, and allows for installation of the tape in a single operation. Table 10 gives the formulation of a typical butyl hot-melt sealant.

### Polyisobutylene

As a homopolymer, polyisobutylene (PIB) is permanently tacky. Most of the PIB used in



Fig. 5.

**Table 10. Butyl Hot-Melt Sealant (Black, Hot Applied).**

	<i>lb</i>	<i>% weight</i>
Butyl rubber, cross-linked	100	27.8
Carbon black (Statex RH)	100	27.8
Naphthenic rubber process oil	120	33.3
Terpene-phenolic resin	40	11.1
Total	360	100.0
lb/gal	9.5	
Nonvolatile, %	99	

sealants is employed in the modification of other sealants or tapes, primarily of the butyl type. The remainder is used in bedding compounds in the glazing industry, usually as part of a combination glazing system.

The lower molecular weight grades of PIB are used to modify butyl caulks; the higher molecular weight grades containing butyl elastomers are used in butyl tapes. Both grades go into PIB bedding compounds. Small amounts of PIB are used in the formulation of insulated glass sealants.<sup>102</sup>

### Hypalon

Hypalon, Dupont's chlorosulfonated polyethylene, finds modest use as a sealant for curtain walls, precast panels, exterior glazing, and roof joints.<sup>27</sup> It possesses not only the good mechanical properties of neoprene, but also excellent color stability, exterior durability, and ozone resistance. Shortcomings as a single component sealant are its relatively poor package stability, extended cure time to reach ultimate elastomeric properties, and relatively high shrinkage from solvent evaporation. Also, the complex curing system may result in excessive post-hardening.

Hypalon caulks are produced primarily as gun-grade compositions, packed in cartridges or in bulk. A typical formulation is shown in Table 11. The cure system comprises tribasic lead maleate (metal oxide source and acid acceptor) and rubber chemical accelerators MBTS and Thiuram M.

### Neoprene (Polychloroprene)

Cured neoprene compositions have excellent elastomeric properties as well as good oil,

**Table 11. Hypalon-Based Sealant (Gun Grade, White).**

	<i>% weight</i>
Hypalon 40	1.7
Hypalon 30	15.7
Chlorinated paraffin (low viscosity)	17.5
Fibrous talc	2.6
Thixotropic agent	2.6
Silica, hydrated, precipitated	5.2
Titanium dioxide (rutile)	14.0
Talc	8.8
Tribasic lead maleate	7.0
Hydrogenated rosin	0.3
2-Mercaptobenzothiazole	0.2
Tetramethyl thiuram disulfide	0.1
Xylol	10.4
Dibutyl sebacate	9.3
Petroleum plasticizer	2.9
Isopropyl alcohol	1.7
Total	100.0
lb/gal	10.9
Nonvolatile, %	88

chemical, ozone, oxidation, and heat resistance, good modulus, exterior durability, and abrasion resistance, but poor initial color and color stability and extended cure time when compounded for gunning. Applications are usually related to oil and chemical resistance, e.g., chemical plant service, automotive, marine, concrete pipe seals, and, to a limited extent, lubricant-adhesives for preformed neoprene highway joint seals.

Both one-part and two-part neoprene sealants are made most commonly using general purpose neoprenes of the GN and W types. Two-part compositions contain 25–30% neoprene plasticized with materials such as dioctyl sebacate or resinous plasticizers, stabilized with phenolic antioxidants, filled with reinforcing pigments such as carbon black and hard clays, and modified with cure-rate regulators and acid acceptors such as zinc oxide and magnesium oxide. Cure accelerators such as polyamines (i.e., tetraethylene pentamine) are used at 5–10 phr based on neoprene.<sup>28</sup> Heat-reactive phenolic resins are also effective. One such composition is shown in Table 12.

One-part compositions contain up to 35% neoprene. Storage life is extended by reducing the levels of curing agent and by dilution with

**Table 12. Neoprene-Based Sealant.**

<i>parts by weight</i>	
<b>Component A</b>	
Neoprene (Type W)	100
Magnesium oxide	4
Antioxidant	2
Calcium carbonate	150
Petroleum process oil	30
Amine-modified bentonite	3
Zinc oxide	<u>5</u>
Total, Component A	294
<b>Component B</b>	
Butyl phenol-formaldehyde resin (heat reactive)	45
Xylol	115
Zinc oxide	<u>7</u>
Total, Component B	167
lb/gal (blended)	11.5
Nonvolatile (blended), %	80

solvents such as xylol down to as low as 55% NV.

Other types of neoprene-containing sealants include a neoprene/Hypalon gun-grade caulk and a pressure-sensitive neoprene foam tape for mounting molding and trim on autos, boats, and trailers.

### SBR and Miscellaneous Elastomers

Elastomers used to a minor extent as the principal binder in sealants include styrene-butadiene rubber (SBR), nitrile rubber, and reclaim rubber.<sup>102</sup>

**SBR.** This elastomer provides good tack and ease of compounding when used. Formulation is in the 12–15% range, along with modified rosin for increased tack and stabilizers for UV and ozone resistance. Because of the high solution viscosity of SBR, large quantities (35–40%) of solvents, such as xylol, are required to achieve satisfactory extrusion properties in a gun-grade compound. Consequently, the resulting sealant has considerable shrinkage. Weathering characteristics are poor. An SBR sealant composition is shown in Table 13.

**Nitrile Rubbers.** These require high solvent levels to produce gunnable sealants, hence are little used. Reclaim rubber goes into asphaltic sealants.

**Table 13. Styrene-Butadiene-Based Sealant.**

<i>% weight</i>	
Styrene-butadiene rubber	12
Polymerized rosin	19
Hydrogenated rosin, methyl ester	2
Aromatic plasticizer	2
Clay	17
Fibrous talc	10
Toluol	26
Xylol	<u>12</u>
Total	100
lb/gal	9.5
Nonvolatile, %	60

**Thermoplastic Elastomers.** These are styrene-butadiene-styrene block copolymers which may have utility in hot-melt sealants. They process more easily than conventional SBR.

**PVC Pressure-Sensitive Tapes.** Formulated PVC plastisols are used in automotive applications. A pressure-sensitive adhesive-coated closed-cell PVC tape has replaced butyl glazing tape in some glazing applications.<sup>29,30</sup> Other applications include automotive, trucks and trailers, mobile homes, steel building erection, metal door gasketing, and sound deadening. Both single-face and double-face tapes are available in various thicknesses, widths, and densities. The pressure-sensitive adhesive is believed to be of the acrylic type.

PVC foam tapes form compression seals in combination glazing with polysulfide, silicone, or acrylic sealants. Elongation and resistance to compression set are excellent, along with good peel strength. The PVC foam cells must not interconnect or there may be wicking of water. PVC tapes are easier to place than conventional butyl tapes, and reportedly cheaper to install than gun-grade caulks or bedding compounds.

### Acrylic Solution

Acrylic solution caulks have been used in glazing and small-joint industrial sealing for over 15 years. The original compounds (at 90% NV) were extremely difficult to extrude at room temperature; cartridges had to be warmed to 120°F before gunning. However, this acrylic

**Table 14. Acrylic Solution Sealant (Room Temperature Application, Gun Grade, Natural Shade).**

	<i>lb</i>	<i>gal</i>
Acrylic solution polymer (83% NV)	545	62.8
Xylol	75	10.3
Pine oil	6	0.6
Ethylene glycol	9	1.0
Calcium carbonate, fine	422	18.7
Fibrous talc	17	0.7
Talc	96	4.3
Silica, pyrogenic	28	1.6
Total	1,198	100.0
lb/gal	12	
Nonvolatile, %	84.5	

sealant has excellent adhesion to common construction surfaces without primers, is nonstaining, and has excellent durability and color permanence. While extensibility is good, recovery is poor as the polymer is not elastomeric. Later acrylic sealants have been formulated at lower solids so as to allow extrusion at temperatures of 50–60°F. This feature is beneficial to applicators but, if overdone, can adversely affect shrinkage and durability properties.

A typical acrylic sealant (Table 14) contains about 37–40% acrylic polymer solids pigmented with calcium carbonate, talc, and fumed silica as a thickening and rheological control agent.<sup>31</sup> Other ingredients include pine oil as a pigment dispersant and penetrating agent for oil or grease on the joint surfaces, ethylene glycol for fumed silica activation, and xylol for viscosity control and extrusion ease. The high solvent content (10–15%) can cause considerable shrinkage, moderated somewhat by the slow solvent release of the system, resulting in sufficient stress relief to overcome joint distortion.

Acrylic solution caulks are available in caulking cartridges or in bulk. Usage is mostly in industrial sealing and glazing, including curtainwall joints, concrete roofs, masonry panels, and metal-to-masonry joints such as flashing, skylights, etc.<sup>32,33</sup>

### Acrylic Emulsion

Acrylic emulsions are easy to apply, adhere well to most construction joint surfaces, clean

**Table 15. Acrylic Emulsion Sealant (Gun Grade, White).**

	<i>lb</i>	<i>gal</i>
Acrylic solution polymer (55% NV)	430.2	48.2
Nonionic surface active agent	9.5	1.0
Sodium polymetaphosphate (anionic)	10.7	0.5
Polymeric plasticizer	124.2	14.9
Mineral spirits	26.9	4.1
Aqueous dispersant, polyacrylate type	1.3	0.1
Calcium carbonate, fine	692.1	30.7
Titanium dioxide (rutile)	17.7	0.5
Total	1,312.6	100.0
lb/gal	13.1	
Nonvolatile, %	83	

up readily, are nonbleeding and nonstaining, and dry rapidly so that they can be painted soon after application. They have low shrinkage, excellent flexibility, fair recovery, and excellent UV resistance and color retention.<sup>37,38</sup>

A typical gun-grade acrylic emulsion sealant (Table 15) contains about 18% acrylic polymer solids and 9–10% of a polymeric plasticizer. Sodium polymetaphosphate is a primary pigment dispersant aided by a water-soluble polyacrylate. A nonionic surfactant acts as a wetting agent and emulsifier. Often small amounts (up to 2%) of glycols are included for additional freeze-thaw stability. Mineral spirits (about 2%) retards skin formation. Acrylic emulsion caulks are used indoors as bathtub caulks, baseboard and trim seams, and outdoors for glazing, masonry joints, and roof and siding joints.

### Polyvinyl Acetate

Sealants and caulks based on vinyl acetate homo- and copolymers have been on the market since the late 1950s. Use of these lower-performance materials has been mostly in residential areas—bathtub caulking, wall tile joints, wallboard joints, etc. Latex caulks based on polyvinyl acetate plasticized with dibutyl phthalate, or on one of the newer vinyl acetate-acrylic emulsion copolymers, have the same ease of application as the acrylic emulsion caulks but are less flexible, harden on aging, and have inferior exterior durability.<sup>102</sup>

A typical polyvinyl acetate caulk, as shown in Table 16, contains about 25–28% copolymer solids, with surfactants, modifiers, and pig-

**Table 16. Polyvinyl Acetate-Based Sealant (Tub and Tile Caulk, White, Low Shrinkage).**

	<i>lb</i>	<i>gal</i>
Vinyl acetate copolymer emulsion (65% NV)	537	59.0
Xylol	9	1.3
Hydroxyethyl cellulose solution (QP 30,000 grade, 2.5% NV in water)	125	15.0
Propylene glycol	33	3.8
Ultramarine blue	0.3	0.01
Titanium dioxide (rutile)	148	4.2
Calcium carbonate, fine	247	11.0
Aluminum silicate	123	5.7
Total	1,222.3	100.0
lb/gal	12.2	
Nonvolatile, %	74	

mentation generally similar to the acrylic emulsion caulks previously described. Total solids are as low as 70% NV; the potential for severe shrinkage always exists, although it is reduced through utilization of some of the new high solids vinyl acetate terpolymer emulsions.

### Polysulfides and Polymercaptans

**Polysulfide Sealants.** Liquid polysulfide polymers are the base of polysulfide sealants, the workhorse elastomeric sealants used in construction, glazing, marine, and aircraft applications for over 35 years.<sup>40-42, 84</sup>

Polysulfide sealants are now available in one-component as well as two-component form, and as gun-grade materials, packed in cartridges or bulk. They are elastomers, expanding and contracting with joint movement; adhesion is good, with satisfactory resistance to water, dust, chemicals and other contaminants or aggressive atmospheres. Hardness can be varied from that of soft rubbers (Shore A = 20) for curtain-wall sealing and high-rise glazing, to hard rubbers (Shore A = 50+) for pour-in-place floor joints and concrete pavement joints which must resist penetration and standing water. Performance life of 20 years or more can usually be expected.

The first manufacturer of liquid polysulfide polymers (LP polymers) was Thiokol Chemical Corp., Trenton, NJ. Most LPs for sealants are condensation polymers of *bis*(2-chloro-

ethyl) ether with sodium polysulfides; small quantities of 1,2,3-trichloropropane are used to produce branching of the LP polymer chains. The final product is a thiol-terminated polyformal with strategically located disulfide linkages.<sup>43</sup> The two LPs most used for sealants have the following characteristics:

	<i>LP-2</i>	<i>LP-32</i>
Mol % cross-link <sup>a</sup>	2	0.5
Molecular weight	4000	4000
Viscosity, poise	400	400
% SH	1.75	1.75

<sup>a</sup>Mol % of 1,2,3-trichloropropane used in manufacture.

The LP polymers are usually cured by oxidation using higher-valence-state metal oxides or peroxides. (Dichromate and manganese dioxide cure systems are used in aircraft systems.) Oxides such as lead dioxide react with the mercaptan groups to form higher polymers as well as crosslinks through disulfide bridges. Cure is accelerated by sulfur and water, and retarded by stearic acid.

Lead dioxide has traditionally been the preferred curing agent, but it cannot be used in white or light-tint compositions. Other curing agents which have been used are manganese dioxide, tellurium oxide, barium peroxide, calcium peroxide, zinc peroxide, and dibutyl tin oxide. Silane adhesion promoters are often utilized in polysulfide sealants.<sup>51</sup>

Lead is toxic; skin contact must be avoided.

**Two-Component Polysulfide Sealants.** Many formulations of two-component polysulfide sealants are available. All have a base component containing the LP polymer and an activator component containing the curing agent. (Automotive windshield sealants, formerly important in the industry, have two activator components.)

A typical construction sealant base composition contains 35-50% LP polymer. Chlorinated terphenyl or chlorinated paraffin were formerly included as an extender to lower cost at little sacrifice in elastomeric properties. However, for health reasons, they have been replaced by phthalate plasticizers. The plasti-

cizer also improves working properties and plasticity. Phenolic resins or epoxy resins are added at the 2–3% level to improve adhesion. Small amounts of stearic acid and sulfur (less than 1%) are used to control the rate and extent of polysulfide cure. Pyrogenic silica or amine-modified bentonite clays, or combinations of the two, are used as thickeners, maintaining slump resistance in vertical joints while the activated system cures. Pigments are chosen which reinforce the rubber while having no adverse effect upon cure. Coated calcium carbonates are the most popular, together with calcined clays and rutile titanium dioxide. Black compounds use good quality carbon blacks such as SRF (see Table 17).

Two-component polysulfide sealants cure to 80–90% of their final strength, adhesion, and elastomeric properties within 16–24 hours.<sup>78</sup> While satisfactory overall, they do have deficiencies. Although they are always supplied in premeasured components, accurate and complete dispersion on the job is essential. Cure

rate is accelerated by high temperatures and humidities, and vice versa. Joints must be scrupulously clean to obtain the best adhesion. Primers are available for use on unsound surfaces, particularly masonry or stone. These are often based on chlorinated rubber solutions, with or without silane adhesion promoters.

Two-component polysulfides are used in industrial construction service: curtainwall sealing; building expansion and contraction joints; precast concrete construction joints; combination glazing; insulated glass sealing; highway, airfield, and bridge joints, canal and inland waterway joints; automotive windshields; aircraft construction and fuel-tank sealing; and various marine construction and repair joints.

### One-Component Polysulfide Sealants.

One-component polysulfide sealants, introduced in 1962, are now made by several companies. They are advantageous in that no field measurement or mixing is required, quality is factory-assured, material loss is minimized, and working time and pot life are not problems as they are with two-component materials.

These materials are formulated in a manner similar to that of two-part systems, with some important differences. The curing agent is an alkali oxide such as calcium peroxide (about 2%) which, upon moisture activation, initiates the LP polymer chain extension and crosslinking reactions. For practical package stability (six months minimum in sealed, aluminum foil lined cartridges), the use of bone-dry ingredients and the complete exclusion of moisture during processing and packaging is essential. Moisture scavengers, such as molecular sieves or barium oxide, are often included as insurance. The total composition contains about 25–35% LP polymer (LP 2 or 32) and about 4–6% aromatic solvent (such as toluol) for improved gunning. A suggested formulation for a one-component sealant is shown in Table 18.

One-component polysulfides skin rapidly at relative humidities above 50%; the remainder of the reaction proceeds slowly into the compound at a rate dependent on temperature, relative humidity, and the ratio of joint width to depth. Cure is slow, reaching about 50% of ultimate properties in seven days—often as long as 30 days if humidity is low.<sup>45-47,95</sup>

**Table 17. A Two-Component Polysulfide-Based Sealant (Gun Grade, Gray).**

	lb	% (weight)
<b>Base</b>		
Polysulfide polymer, liquid	100	54.42
Phthalate plasticizer	20	10.89
Calcium carbonate, precipitated, surface treated	35	19.05
Titanium dioxide, rutile	10	5.44
Carbon black, furnace	5	2.72
Stearic acid, single pressed	1	0.54
Organic-modified bentonite clay	3.0	1.64
Fumed silica	2.5	1.36
Phenolic resin	5	2.72
Gamma-aminopropyltriethoxy silane	0.15	0.08
Sulfur, sublimed	0.1	0.05
Toluene	2	1.09
Subtotal, base	183.75	100.00
<b>Activator</b>		
Lead dioxide, technical	7.5	50.00
Stearic acid	0.75	5.00
Dibutyl phthalate	6.75	45.00
Subtotal, activator	15.00	100.00
lb/gal, blended	13.5	
Nonvolatile, %	99+	



**Table 18. Polysulfide-Based Sealant (Single-Component, Gun Grade, White).**

	% (weight)
Polysulfide liquid polymer (LP-32)	50
Epoxidized soya oil	4
Pyrogenic silica	2
Calcium carbonate, surface treated	5
Titanium dioxide, rutile	22
Hydrated lime	2
Synthetic zeolite	2
Calcium peroxide	4
Phthalate plasticizer	2
Gamma-aminopropyltriethoxy silane	1
Toluol	4-6
Total	100
lb/gal	12
Nonvolatile, %	96

Note: Manufactured and packed under anhydrous conditions.

**Polymercaptans.** Mercaptan-terminated polypropylene oxide polyethers for sealant use were developed in the 1960s. Formulation and curing procedures are similar to those used with the LP polymer polysulfides since both make use of the thiol group.

The sealant grade material had a molecular weight of 5000–6000. Considerable interest was shown in this material by sealant producers because of its lower price than polysulfide.

However, polymer quality and cure rates were not reproducible batch to batch, and field experience showed that chemical resistance and dynamic sealant properties were inferior to those of polysulfides. Second generation polymercaptans were introduced in 1974.<sup>81, 82, 94</sup>

### Polyurethanes

Polyurethanes are the most versatile polymer systems used to formulate elastomeric sealants. Polyurethane sealants are sold both as two-component and one-component gun-grade compositions, packed in cartridge or in bulk. Applications are similar to those of the polysulfides, including the insulated glass markets and sealing automotive windshields.

Most polyurethane sealant systems are based on the reaction of polyhydroxy materials (and diamines) with polyisocyanates in situ to produce a polyurethane (or urethane-urea) rubber. By varying backbone compositions, NCO/OH ratios, catalyst content, etc., a wide range of

compositions and properties are made available by the formulator to the end user. Earlier urethane compositions had excessively high moduli; cohesive strength was far greater than strength of adhesion to the joint substrate, with resulting adhesive failure. Also, adhesion was destroyed readily after exposure to UV through glass. Primers are now utilized to improve adhesion. In addition, compositions have been modified to give lower crosslink densities and moduli.

Urethane sealants have good elongation and recovery, excellent abrasion resistance and tear strength; their resistance to indentation make them the preferred compounds for floor joint compounds, highway and airfield joint materials, and preformed gasket seals in clay and concrete pipe. Low temperature performance (to below  $-40^{\circ}\text{C}$ ) is superior to that of the polysulfides.<sup>52, 53, 93, 96</sup>

The polyhydroxy components of urethane sealants are mostly hydroxyl-terminated saturated polyesters or polyethers. Most polyesters used in urethane sealants have been standard condensation products of dibasic acids (such as adipic acid or phthalic anhydride) with glycols and triols (such as propylene glycol, glycerin, or trimethylol propane). Polyester-based urethane sealants are hard and tough, have relatively good adhesion in joints, but are deficient in hydrolytic stability and exterior durability.

Polyether polyols are usually preferred as the hydroxyl-rich components of urethane sealants. These are normally polypropylene oxide condensates with molecular weights in the 400–4000 range, hydroxyl-terminated. Triols are incorporated in minor proportion to provide for crosslinking. Compared to polyesters, polyether urethanes have superior hydrolytic stability, lower moduli, but somewhat inferior adhesion.

The most common polyisocyanate used in urethane sealant production is toluene diisocyanate (TDI). The TDI is usually prereacted to give an isocyanate-terminated prepolymer. Other aromatic polyisocyanates used in sealants include diphenylmethane diisocyanate (MDI) and polymethylene polyphenylene isocyanate (PAPI). All of the aromatic polyisocyanates contribute to yellowing of urethanes on exposure to light.

Nonyellowing urethane sealants can be made using aliphatic or cycloaliphatic polyisocyanates or with compounds where the NCO group is removed from the benzene ring by at least one methylene group. These include hexamethylene diisocyanate (most frequently as its less toxic biuret with water), methylcyclohexyl diisocyanate, dimer acid diisocyanate, and xylene diisocyanate. Since these materials are considerably more expensive than TDI, usage is limited.

The isocyanate-terminated prepolymers used in most urethane sealants incorporate polyester, polyether or other polyol building blocks. Curing to elastomeric compositions is achieved in two ways: two-component, by the addition of a hydroxyl-rich coreactant (polyester or polyether); or one-component, by water absorption followed by polyurea formation with elimination of carbon dioxide.

#### Two-Component Polyurethane Sealants.

As with polysulfides, many formulations of two-component urethane sealants are available to suit the wide varieties of applications and product qualities expected by users. Most commonly, the NCO/OH equivalent ratio is about 1.05–1.10. One component is a liquid isocyanate-terminated prepolymer, pigmented and filled with titanium dioxide (if white), calcium carbonate, talc, or silica. The second component is a hydroxyl-terminated polymer, often pigmented as well, containing small amounts of a catalyst such as methylene dianiline (which also reacts with isocyanate and serves as a flow-control agent). Ingredient mixing is done with heat under anhydrous conditions for maximum stability. These compounds have polymer contents in the 50–70% range. Component mixing in the field must be very thorough. Pot life range is 1–4 hours; substantially all of the elastomeric properties are achieved within 24–48 hours. A typical formulation is shown in Table 19.

Their applications in industrial construction include vertical joints with high movement requirements, and horizontal or floor joints where their hardness, toughness, abrasion resistance, and resistance to indentation are important. They are suitable for insulated glass sealants.

Rapid-cure characteristics make the ure-

**Table 19. Polyurethane-Based Sealant (Two-Component, Gun Grade, White).**

	<i>parts by weight</i>	<i>%</i>
<b>Component A</b>		
Polyethylene glycol–isocyanate prepolymer (2.6% free isocyanate)	100	100
<b>Component B</b>		
Antioxidant	0.65	0.5
Polypropylene glycol (MW = 2000)	62	47.3
Titanium dioxide-rutile	7.86	6.0
Calcium carbonate filler	49	37.2
Nonsag agent	10.4	8.0
Tin catalyst	<u>1.81</u>	<u>2.0</u>
Total	131.72	100.0
lb/gal (blended)	11.5	
Nonvolatile, %	99+	

thanes good candidates for windshield sealants. They are also used in highway and airfield sealing, aircraft construction, and marine applications.

#### One-Component Polyurethane Sealants.

Isocyanate prepolymers with NCO equivalent weights of 1000–2000 are used in the formulation of one-component urethane sealants. A typical gun-grade compounds may contain 30–60% of prepolymer, pigmented with titanium dioxide, calcium carbonate, and silica, with up to 5% of dry toluol for easier gunning. Compounds may also contain molecular sieves to absorb unremoved water for improved compound stability. As with one-component polysulfide sealants, manufacture of the compound is carried out with dry ingredients under vacuum and heat so as to eliminate all traces of water. One suggested formulation is shown in Table 20.

Since they cure by moisture absorption, one-component urethane sealants have joint restrictions and delayed cure characteristics similar to those of one-component polysulfides, except that urethane sealants cure somewhat faster in similar joints because of greater moisture permeability. Materials are available with package life of up to one year when well sealed from moisture. Catalysts such as 1,2,4-trimethylpiperazine can speed cure, but at a sacrifice in package life.

A method can be used for preparing one-

**Table 20. Polyurethane-Based Sealant, Moisture Curable (Single Component, Gun Grade, White).**

	% weight
Titanium dioxide, rutile	2.0
Calcium carbonate, fine	34.5
Silica, precipitated	6.0
Molecular sieve	1.0
Isocyanate prepolymer <sup>a</sup>	30.0
Phthalate plasticizer	23.0
Organosilane, epoxy functional	1.0
UV absorber	0.5
Toluol	2.0
Total	100.0
lb/gal	11.5
Nonvolatile, %	98
<sup>a</sup> Prepolymer (3% unreacted isocyanate):	
Polypropylene glycol diol (EW = 1000)	67.7
Polypropylene glycol triol (EW = 1600)	19.1
Toluene diisocyanate	13.1
Dibutyl tin dilaurate	0.1
	100.0

NCO/OH = 1.9

component sealants which reduces moisture sensitivity during manufacture and yields improved package stability and wet adhesion. The polyol is chain-extended with TDI to a molecular weight of 10,000–15,000 and then stoichiometrically end-capped with  $\gamma$ -aminopropyltrimethoxy silane to react all of the free NCO groups. In a pigmented one-component urethane sealant, this prepolymer cures by hydrolysis of the methoxy groups and siloxane polymerization.

### Silicones

Silicone rubbers are outstanding in resistance to high temperature, low temperature flexibility, and exterior durability. Two-component types have been developed with both heat cured (HTV) or room-temperature (RTV) cured vulcanization.<sup>75-77, 101, 104, 105</sup>

Silicone sealants have been used in a number of applications in construction, industrial, and consumer markets. The versatility of silicone systems is derived from the range of high-performance properties. These properties include ease of application with a wide range of rheological properties (including nonsag and pourable grades), rapid cure, excellent elastomeric properties (including extension/compression and high recovery), good thermal stability, and

good UV, ozone, and chemical resistance with low shrinkage. Also, silicone based materials display good release and electrical insulation properties. Silicone sealants can be compounded into low, medium, and high modulus one-part RTV sealants. Table 21 shows basic low, medium and high modulus formulations.

The RTV cure of silicone sealants usually involves the hydrolysis of dimethyl siloxane intermediates and their condensation to polysiloxanes. Crosslinking occurs through condensation of trifunctional organosilanes, usually catalyzed by organometal soaps such as dibutyl tin dilaurate. Polysiloxanes containing vinyl groups can be crosslinked by organic peroxides. A variety of one- and two-component silicone elastomers can be formulated, depending on application and performance requirements.<sup>101, 105</sup>

**One-Component Silicones.** The liquid silicone prepolymers used in one-component sealants are usually methyl-substituted polysiloxanes having more than two blocked, hydrolyzable end groups. These groups may be acetoxy, ketoxime, alkylamino, or benzamido. When the composition is extruded into a joint

**Table 21. Silicone Sealants.**

Component	%
Basic Low Modulus Formulation (N-Methyl Acetamide Chain Extender and Diethylhydroxylamine Crosslinker) <sup>104</sup>	
Silanol polymer (4000 cs)	46.0
Calcium carbonate	50.0
Methyl vinyl di(N-methyl acetamido)silane	3.0
Aminoxy siloxane copolymer	0.7
Basic Medium Modulus Formulation (oxime)	
Silanol polymer (80 mcs)	60–80
Silicone plasticizer	5–20
Fumed silica (treated and/or untreated)	2–6
Calcium carbonate (treated and/or untreated)	20–30
Oxime crosslinker	5–7
Tin catalyst	0.05–0.1
Basic High Modulus Formulation (Acetoxy)	
Silanol polymer (20 mcs)	80–85
Fumed silica (treated and/or untreated)	6–10
Acetoxy crosslinker	5–7
Tin catalyst	0.05–0.1

and exposed to atmospheric moisture, the end groups are hydrolyzed off as acetic acid, etc. Because of the odor of acetic acid and its corrosiveness to metals, limestone, and cement, the ketoxime-blocked silicones are preferred. The unstable Si—OH segments rapidly condense, forming Si—O—Si bonds to give a three-dimensional structure. The skin is tack-free within 30 minutes; the rubber continues to cure from the outside in at a rate depending on humidity and joint dimensions.

Silicone sealants of this type are available as colorless (translucent) compositions if desired. Silicone polymer content is in the 60–70% range (40–50% polysiloxane plus up to 20% dimethyl silicone or methylphenylsilicone plasticizer). Pigments and fillers include titanium dioxide, silicas, calcium carbonate, or dried clays. Pyrogenic silicas are used for rheological control to produce nonslump sealants.

Like the one-component polysulfides or polyurethanes, the one-component silicones must be protected from moisture during manufacture and storage. However, package stability of the silicones is superior. If a cartridge is only partially used, the plug of cured rubber which forms in the tip retards further moisture penetration.

The wide range of properties has expanded the commercial use of one-component silicone sealants. Examples of industrial applications include:

- Form-in-place gaskets for automotive areas such as valve covers, oil pans, thermostats, rear axle covers, automatic transmission housing, and tail light assemblies;
- Automotive adhesive applications such as adhering rear view mirrors;
- Gaskets for household appliances such as dishwashers, washing machines, vacuum cleaners, electric steam irons, etc.;
- Aerospace gaskets for windows and doors;
- Electronic encapsulation of connectors and terminals;
- Conformal coatings to protect circuit boards and electrical components;
- Fabric coatings;
- Secondary seal for insulating glass.

Because of their weathering and movement capabilities, and adhesive qualities to glass and

metal substrates, silicone sealants are widely used in such construction applications as expansion joints, perimeter sealing, control joints, nonstructural glazing, and structural glazing.<sup>58-62, 99</sup>

Due to their dependability, versatility, and durability, silicone sealants have found use for the consumer market. These uses include bathtub caulk, auto sealants, windshield sealants, window sealants, high temperature gaskets, and general household glues and sealants.

### Two-Component Silicone Sealants.

These products contain, in the larger component, a hydroxyl-terminated polysiloxane and a crosslinker such as ethyl orthosilicate. The activator part is an organometal catalyst, e.g., dibutyl tin dilaurate in paste form. Upon mixing, cure takes place in the entire mass.

The two-part silicones are used in aircraft and electrical potting and encapsulation. Industrial and construction applications include secondary seals for high performance insulating glass units and structural glazing, respectively.

For special applications, the pendant methyl group along the polymer chain can be replaced with other organic groups. The common substitutions are the phenyl, cyanoethyl, and trifluoropropyl groups. Partial substitution of the methyl groups with phenyl can give silicone sealants improved low temperature properties and oxidation resistance. The improvement of in-place temperature (service temperature) utility will be a function of the percent phenyl in the polymer. For example, the substitution of 5.3 mole percent diphenylsiloxy units will lower the resultant brittle point of the sealant from  $-85^{\circ}\text{F}$  to  $-165^{\circ}\text{F}$ . The addition of a polar group such as trifluoropropyl or cyanoethyl will increase the solvent resistance of the cured silicone sealant. These polar groups make silicone polymers incompatible with nonpolar organic fuels and oils, giving them fuel resistance. Again, the exact solvent resistance is a function of the percent of trifluoropropyl in the polymer.

### Fluoropolymers

The expensive fluoroelastomers are used in small volume in high temperature and fuel-resistant seals in military aircraft, as well as in

automotive, chemical processing, and electrical applications. The principal fluoroelastomers are copolymers of vinylidene fluoride and hexafluoropropene. Cure is believed accomplished in a two-component system by extraction of HF by reaction with diamines, such as hexamethylene diamine carbamate, activated with magnesium oxide and dibasic lead phosphite.

Cured fluoroelastomers can withstand prolonged exposure to high temperatures and retain their elastomeric, mechanical, chemical, and electrical properties better than other elastomers. Continuous service at 450°F is common; intermittent exposure at 600°F is possible. Although resistance to compression set is excellent at 400–450°F, low temperature properties (including compression set) are poor, compared to silicones and fluorosilicones.

Phosphonitrilic fluoroelastomers have a phosphonitrilic backbone with trifluoroethoxy and heptafluorobutoxy side groups. The rubbers are useful in the temperature range from –100°F to 300°F, are solvent-resistant and nonflammable.

## SEALANT SELECTION, JOINT DESIGN, AND INSTALLATION

In determining the appropriateness of a sealant or caulk for an application, many factors need to be considered. The generic polymer technology, the physical form, sealant classification, specifications and performance properties are all important features of a sealant or caulk. Table 22 outlines some basic performance properties of the sealant types reviewed in this chapter. As seen in Table 22, most of these sealant types are utilized in construction applications. As described earlier in this chapter, sealants and caulks can be classified in low, medium, and high movement categories, and selection is primarily decided on the basis of movement capability, adhesion, life expectancy, and material cost. Table 23 reviews the typical applications for these types of sealants and caulks.

The following is a description of the selection of the appropriate sealant, then proper joint design and installation for construction sealant/caulk applications.

### Sealant Selection

Sealant joints cannot be designed until a decision is made as to what sealant we desire to utilize. Its ability to expand and contract remains the most important factor in that decision. Major manufacturers indicate the movement capacity of a sealant as plus or minus a certain percentage of its designated width.

For instance, a 1" wide joint utilizing a sealant with capacity of  $\pm 25\%$  indicates that the sealant can withstand the joint's compression to  $\frac{3}{4}$ " or its expansion to  $1\frac{1}{4}$ " without either the adhesive failure of its bond or the cohesive (tearing) failure of the sealant.

In selecting the proper sealant for a specific situation, consideration must also be given to such characteristics as its service life, hardness, cure time, application parameters, adhesion to various substrates, weather, stain, and chemical resistance, and rate of recovery. (See Tables 22 and 23.)

### Movement Capability

**Low Movement Sealants (Caulks).** These include polybutene, polyisobutene, and oil and resin-based caulks. These low cost sealants have an approximate joint movement capacity of only  $\pm 5\%$ , a slow rate of cure (120 days), a low Shore A hardness, a relatively short service life (approximately 6 or 7 years on average), and only modest weather or chemical resistance. Therefore, low movement sealants are primarily utilized in static joints having minimal exterior exposure.

Applications of low movement sealants include perimeter joints of residential door and window frames, siding, or interior duct work. Generally, they require a minimum amount of surface preparation, have good adhesion characteristics, and are supplied in one-component cartridges.

**Medium Movement Sealants.** These exhibit higher performance properties. The latexes and butyls have a movement capacity of  $\pm 7.5\%$ . Hypalon, neoprene, and solvent-release acrylics have a movement capacity of  $\pm 12.5\%$ . Cure time is about 5 days for latexes, 30 days for Hypalon and neoprene, 120 days for butyls. Service life is 10 years for most me-

Table 22. Sealants Selection and Application Guide (Sealant, Caulk, Glazing Compound, by Polymer Type).

Properties	Asphalt													
	Bituminous	Oleoresinous	Polybutene	Butyl	Hypalon	Neoprene	Styrene-Butadiene	Acrylic Solution	Acrylic Emulsion	Polyvinyl Acetate	Polysulfide	Polyurethane	Silicone	Fluoropolymer
NV, % by weight	70-90	96-99 +	99 +	74-99 +	85-90	80-85	60-70	80-85	80-85	70-75	90-99 +	94-99 +	98 +	99 +
Weight, lb/gal	9-12	14-20	13-14	10-13	10-11	11-12	9-10	12-13	12-14	12-13	12-15	11-12	10-12	14-16
Max. joint movement, % ±	5	5	5-10	10-15	10-15	10-15	5-10	10-15	5-10	5	25	25-40	25-50	10-20
Recovery after joint movement <sup>a</sup>	P	P	NA <sup>b</sup>	F-G	F	P-F	P-F	F	F	P-F	F	G	E	F-G
Shrinkage, %	10-20	4	1	1-20	10-15	10-20	20-30	10-20	10-20	20-25	10	6	2	1
Life expectancy, exterior, yr	1-2	2-10	5-10	5-15	5-15	5-15	3-10	5-20	2-20	1-3	10-20	20+	30+	10-20
Cure type	Evap.	Oxidtn.	Noncure	Evap.	Chem.	Chem.	Evap.	Evap.	Evap.	Evap.	Chem.	Chem.	Chem.	Chem.
Practical service temp. range														
max. °F	150	150	180	200	225	210	180	180	180	150	250	250	400	500
min. °F	0	0	-40	-20	-25	-25	-10	0	0	0	-40	-40	-90	-10
Adhesion to common building materials, unprimed <sup>d</sup>	G	G	G-E	G	F-G	F	F	E	G	F-G	G	G	F-G	F
Components, one-part, two-part, tape	1	1	1,T	1,T	1	1	1	1	1	1	1,2	1,2	1,2	2

<sup>a</sup>E = less than 10% compression set; G = 10-20%; F = 20-30%; P = <30%.<sup>b</sup>NA = not applicable.<sup>c</sup>Mild to severe conditions.<sup>d</sup>Adhesion of all materials improved with suitable primers.

**Table 23. Sealant and Caulk Distribution by Polymer Type and Application.**

Polymer Type	Construction									
	Resid. <sup>a</sup>	Indust. Comm. <sup>a</sup>	Prefab. Housing <sup>b</sup>	Insul. Glass	Auto. <sup>c</sup>	Highway <sup>d</sup>	Airfield Runways	Aircraft Aerospace <sup>e</sup>	Marine <sup>f</sup>	Other <sup>g</sup>
Asphalt, bituminous					X	X	X			
Oleoresinous	X	X	X						X	
Polybutene	X	X	X	X	X					
Butyl <sup>h</sup>	X	X	X	X	X					X
Hypalon	X	X								
Neoprene		X								
Styrene-butadiene <sup>i</sup>		X								X
PVC		X								
Acrylic solution		X								
Acrylic emulsion	X	X								
Polyvinyl acetate	X	X								
Polysulfide <sup>j</sup>	X	X	X	X	X	X	X	X	X	
Polyurethane		X		X	X	X	X	X	X	
Silicone <sup>k</sup>	X	X		X	X	X	X	X	X	X
Fluoropolymer								X		
Others <sup>l</sup>		X								X

<sup>a</sup>Resid. (residential)—home and architectural maintenance and repair. Indust. Comm. (industrial, commercial)—commercial, professional applications, OEM (original equipment manufacture), maintenance, and repairs.

<sup>b</sup>Prefabricated housing, modular housing, mobile homes, recreational vehicles, campers.

<sup>c</sup>Automotive, including truck and trailer, and aftermarket.

<sup>d</sup>Highways, bridges, canals, dams, interior waterways.

<sup>e</sup>Including electrical and electronic sealants for aircraft applications.

<sup>f</sup>Including aftermarket.

<sup>g</sup>Including pipe seals, undistributed electrical and electronic applications, appliances, chemical processing equipment.

<sup>h</sup>Including polyisobutylene.

<sup>i</sup>Including nitrile rubber.

<sup>j</sup>Including polymercaptans.

<sup>k</sup>Including fluorosilicones.

<sup>l</sup>Including telechelic butadiene copolymers, polypropylene, EPDM (ethylene-propylene-diene polymers), poly(isoxazolines), epoxy resins, polyimides.

dium movement sealants but up to 20 years for neoprene.

Sealants having medium performance capability offer a longer life than caulks, along with significantly better performance characteristics, but at a higher price.

Medium movement sealants show versatility. Latex sealants offer compatibility with latex paint in that they are suitable for coating and provide ease of cleanup. This allows them to be used as an interior sealant under paint finishes. Butyl sealants have good adhesion to most surfaces and good resistance to water. This leads to their use in such places as door thresholds, flashing, metal and vinyl siding, and duct end pipe penetrations.

Hypalon sealants offer good UV, ozone, and chemical resistance. These properties allow them to be used in moderately moving exterior joints around doors and windows or concrete panels. Neoprene sealants exhibit compatibility

with asphaltic concrete and bitumen. This property encourages their usage in roadway applications. Finally, solvent-based acrylics have a movement capability of  $\pm 12.5\%$ , minimal shrinkage, high strength, good resistance to weather and chemicals, and excellent recovery of their original shape after compression. These properties, along with a relatively short range of cure (14–21 days) allow them to be utilized in some exterior dynamic joint applications.

**High Movement Elastomeric Sealants.** These include polysulfides, polyurethanes, and silicones.

Polysulfides were the first generation of high performance sealants. They were introduced into the construction market in the early 1950s. However, since the mid-1970s, polysulfides are being displaced as building joint sealants by urethane and silicone products. Polyurethane sealants are the most versatile polymer

systems used to formulate one- and two-part sealants. Nonsag urethane sealants are used for high movement construction joints, while self-leveling, cold-pour-type sealants are used in horizontal traffic applications. Silicones have been used in a number of applications in industrial, consumer, and construction markets. Silicone sealants have widespread use as sealant/adhesives for structural glazing due to their extreme high recovery, movement capacity, and weather resistance. Fig. 6 shows four structural glazing details in which the glass is retained at either two (butt glazing) or four (stopless glazing) edges.

The service life of these sealants is 20 years or more. They have a range of movement from  $\pm 25\%$  (polysulfides) to  $+40/-25\%$  (polyurethanes) to  $+100/-50\%$  (low modulus silicone sealants) extension/compression. Their price can range as much as seven times that of some low movement caulks.

## BACKUP MATERIALS

The primary purpose of the backup material in the joint is to control the depth of the sealant in the joint, thus ensuring the proper shape factor. Another purpose of the backing is to provide support or reinforcement for the sealant material in horizontal joints, such as floors and patios. Depending on the type of construction, the backup material may be already in the joint—for example, the plastic or cork board joint sometimes used in pavement construction.<sup>97</sup>

The backup material must be unaffected by any solvent contained in the sealant. Backup material containing asphalt, coal tar, or polyisobutylene should never be used. These extrudable oils are incompatible with some sealants and may cause loss of adhesion. It is quite possible that these extrudables may cause staining of porous substrates.

Neoprene, urethane, polyurethane, polyethylene foam, cork board, fiberboards, cotton rope, and jute have all been used as backing material. The foams have been the most successful materials because they are quite compressible with very little spread. The foams are readily available in strip form, in both round and rectangular cross sections to fit most joints.

Rubber tubing made of neoprene, EPDM, or butyl is an excellent but expensive backup material. In essence, the tubing acts as a dual system with the sealant, since the partly compressed tubing will also act as a water barrier in case the sealant suffers a loss of adhesion.

Both open- and closed-cell backups are used. The closed-cell backup does not permit any water to contact the sealant but has been a problem where the backer rod is first compressed into the joint. If the rod is punctured during installation, gas will slowly be released into the uncured sealant, causing surface bubbles. This bubbling can be quite conspicuous if the wall is exposed to sunlight on a hot day before the sealant cures. The solution is to use open-cell foam. Open-cell foam is desirable if a one-part sealant that requires moisture activation is used. Here, the sealant will begin curing from both sides. However, the open-cell foam may in time become saturated with moisture and cause adhesion problems or even frost formation and spalling. Properly vented walls would reduce this problem. There is no ideal solution, and the selection of backup material will depend on the sealant used and job site conditions.

A word of caution: outgassing of closed-cell backer rod can be prevented if the installer does not use sharp tools when pushing the rod into place. This will prevent rupture to the rod.

## SPECIFICATIONS

In the selection of a sealant or caulk, the methodology of performance evaluation must be understood. The performance data by the manufacturer must be quantifiable and comparable to other materials. A method must be used to determine the *appropriateness* of a sealant or caulk in a specific application. Test methods and specifications have been established by the ASTM, Bureau of Standards, Adhesive and Sealant Council, and other agencies.

Table 24 lists important U.S. specifications for sealants and caulks; Table 25 lists ASTM test methods for building seals and sealants; and Table 26 is a reference guide for sources of sealant and caulk specifications.



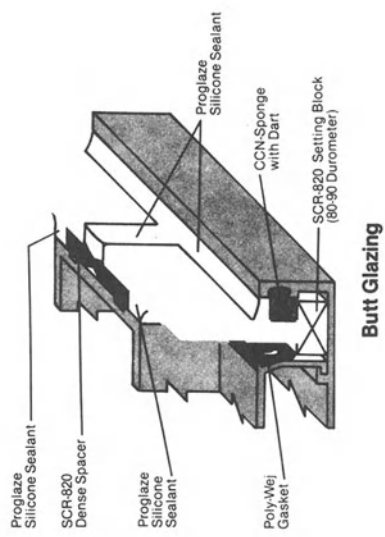
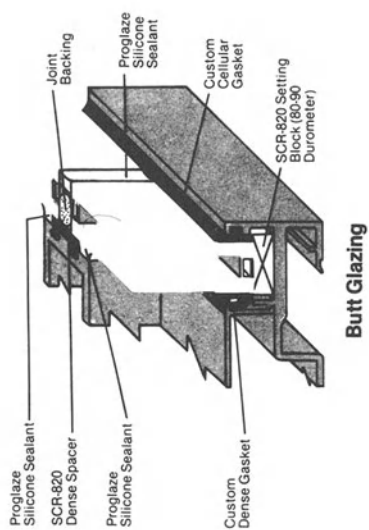
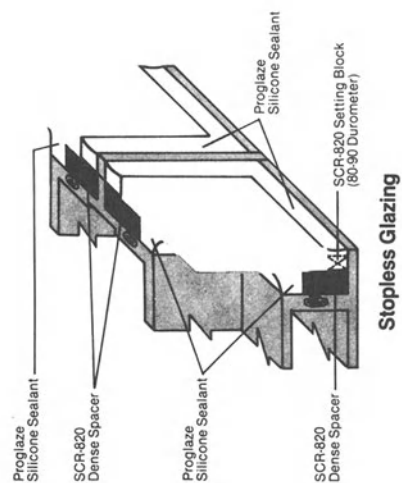
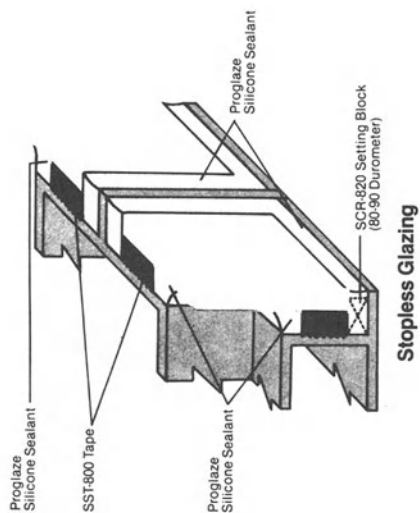


Fig. 6.

**Table 24. Sealant Specifications.****CONSTRUCTION***Federal Specifications*

TT-S-00227E (11/4/69)	Sealing compound elastomeric type, multicomponent (for caulking, sealing, and glazing buildings and other structures)
TT-S-00230C (10/9/70)	Sealing compound elastomeric type, single component (for caulking, sealing, and glazing buildings and other structures)
TT-S-01543A (6/9/71)	Sealant compound, silicone rubber base (for caulking, sealing, and glazing buildings and other structures)
TT-C-598B (3/17/58)	Caulking compound, oil and resin base type (for masonry and other structures)
TT-S-001657 (10/8/70)	Sealant compound, single component, butyl rubber based, solvent release type (for buildings and other types of construction)

*ASTM Specifications*

ASTM C570-72 (reapproved 1984)	Standard specification for oil and resin base caulking compound for building construction
ASTM C669-75 (reapproved 1981)	Specification for glazing compounds for back bedding and face glazing of metal sash
ANSI/ASTM C834-76 (reapproved 1981)	Standard specification for latex sealing compounds
ASTM C836-84	Standard specification for high solids content, cold liquid-applied elastomeric waterproofing membrane for use with separate wearing course
ANSI/ASTM C920-79	Standard specification for elastomeric joint sealants
ASTM C957-81	Standard specification for high solids content, cold liquid-applied elastomeric waterproofing membrane with integral wearing surface

*Insulating Glass*

ASTM E774-84a	Standard specification for sealed insulating glass units
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*AUTOMOTIVE*

AMS-3087E	Compound, insulating and sealing, silicone
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*HIGHWAY/  
BRIDGES,*

	American Association of State Highway and Transportation Officials (AASHTO)
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SS-S-200E(3)	Sealing compounds, two-component, elastomeric, polymer type, jet fuel resistant, cold applied
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*MILITARY SPECIFICATIONS*

MIL-A-46106(2)	Adhesive-sealants, silicone, room temperature vulcanizing, general purpose
MIL-A-46146 (2) AMD 3(MR)	Adhesive-sealants, silicone, RTV, noncorrosivity (for use with sensitive metals and equipment)
MIL-A-47040(1) (1) (MI)	Adhesive-sealants, silicone, room temperature vulcanizing, high temperature
MIL-C-15705A(1)	Caulking compound (liquid polymer polysulfide synthetic rubber formula #112 for metal enclosures)
MIL-C-46867(MI)	Compound, caulking, conductive
MIL-C-47070(MI)	Compound, polyurethane
MIL-C-47113(MI)	Compound, heat sink, silicone
MIL-C-47121(MI)	Compound, sealing, polysulfide rubber
MIL-C-47164(MI)	Compound, plastic polyurethane
MIL-P-47170(1)(MI)	Primer, silicone rubber sealant
MIL-P-47216(MI)	Primer, polyurethane
MIL-P-47275(MI)	Primer, silicone
MIL-S-11030E	Sealing compound, noncuring (polysulfide base)
MIL-S-11031B	Sealing compound, adhesive, curing (polysulfide base)
MIL-S-11388B	Sealing compound for metal container seams

Table 24. (Continued)

**MILITARY SPECIFICATIONS**

MIL-S-12158C(AT)	Sealing compound, noncuring, polybutene
MIL-S-14231C(1)	Sealing compound, joint, two-component, for bolted aluminum or steel petroleum storage tanks
MIL-S-22473D(4)	Sealing, locking and retaining compounds
MIL-S-23586C(3)	Sealing compound, electrical, silicone rubber, accelerator required
MIL-S-2869B	Sealing compound, synthetic rubber, hose cover repair
MIL-S-3105C	Sealing compound, inert (for use in ammunition)
MIL-S-3927C(1)	Sealing compound, thread, polymerizing, room temperature
MIL-S-4383B(2)	Sealing compound, top coat, fuel tank, Buna N type
MIL-S-45180C	Sealing compound, gasket, hydrocarbon fluid and water resistant
MIL-S-46163(1)	Sealing, lubricating and wicking compounds—thread locking, anaerobic, single component
MIL-S-47122(MI)	Sealing compound
MIL-S-47123(1)(MI)	Sealant, ablative, silicone base, room temperature curing and primer
MIL-S-47162(1)(MI)	Sealant, silicone rubber, room temperature vulcanizing
MIL-S-47165(MI)	Sealing compound, high tear strength
MIL-S-47245(MI)	Sealant, electrically conductive
MIL-S-48112(MU)	Sealing compound, butyl rubber sealant (for use with ammunition)
MIL-S-7916C	Sealing compound, thread and gasket, fuel, oil and water resistant
MIL-S-81732(1)(AS)	Sealing compound, electrical, high strength, accelerator required
MIL-S-8516E(2)	Sealing compound, polysulfide rubber, electric connectors and electric systems, chemically cured
MIL-S-8660B(4)	Silicone compound
MIL-S-8784B	Sealing compound, low adhesion, for removable panels and fuel tank inspection plates
<i>Navy</i>	
MIL-C-18225D(3) (ships)	Caulking compound, synthetic rubber base, wooden deck seam application
MIL-C-81947A	Coating compound, thermal insulation, 3 component, intumescent
MIL-S-15204C(2) (ships)	Sealing compound, joint and thread, high temperature
MIL-S-17377D (ships)	Sealing compound, boiler casing
MIL-S-19653A (ships)	Sealing compound (wood beddings) fortified
MIL-S-23498(1) (ships)	Sealing compound, bearing preservation, synthetic rubber base
MIL-S-24340 (ships)	Sealing compound, deck, polyurethane (polyester base)
MIL-S-2912D(1) (ships)	Synthetic rubber compound, acid and oil resistant (for lining battery compartments on submarines)
MIL-S-81733B(2) (ships)	Sealing and coating compound, corrosion inhibitive
<i>Aircraft</i>	
MIL-C-83983 (USAF)	Compound, sealing, fluid resistant
MIL-S-38228(2) (USAF)	Sealing compound, environmental, for aircraft surfaces
MIL-S-7124B	Sealing compound, polysulfide, accelerator required, for aircraft surfaces
MIL-S-88315(1) (USAF)	Sealing compound, aluminum structure, pressure and weather sealing, low density
MIL-S-83318(1) (USAF)	Sealing compound, low temperature curing, quick repair, integral fuel tanks and fuel cell cavities
MIL-S-83430(3) (USAF)	Sealing compound, integral fuel tanks and fuel cell cavities intermittent to use to 360°F (182°C)
MIL-S-83432 (USAF)	Sealing compounds, adhesive bonded structure
MIL-S-8802D(1) AMD2 (USAF)	Sealing compound, temperature resistant, integral fuel tanks and fuel cell cavities, high adhesion

**Table 25. ASTM Building Seals and Sealants Test Methods.**

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1. American Society of Testing and Materials (ASTM C-24)
  2. The 1986 Annual Book of ASTM Standard on Building Seals and Sealants in Volume 04.07
  3. ASTM C-24 Active Technical Committees. The ASTM C-24 Committee was organized in 1959 to develop standards for building seals and sealants. Currently, the following 18 technical subcommittees are identified:
    - C-24.12 Oil and Resin Base Glazing and Caulking Sealants
    - C-24.15 Hot Applied Sealants
    - C-24.16 Emulsion Sealants
    - C-24.18 Solvent Release Sealants
    - C-24.32 Chemically Curing Sealants
    - C-24.35 Structural Sealants
    - C-24.40 Backup Materials
    - C-24.50 Tape Sealants
    - C-24.70 Lock Strip Gaskets
    - C-24.72 Compression Seal Gaskets
    - C-24.80 Building Deck Waterproof Systems
    - C-24.82 Criteria for Evaluation of Sealant Testing Laboratories
    - C-24.83 Statistical Analysis
    - C-24.84 Insulating Glass Sealant Compatibility
    - C-24.85 Sealants for Acoustical Applications (inactive)
    - C-24.86 Solar Collector Seal Applications (inactive)
    - C-24.87 International Standards
  4. List of ASTM C-24 Standards
 

C-510-77 (reapproved 1983)	Test for staining and color change of single or multicomponent joint sealants
C-570-72 (reapproved 1984)	Specification for oil and resin-base caulking compound for building construction
C-603-83	Test for extrusion rate and application life of elastomeric sealants
C-639-83	Test for rheological (flow) properties of elastomeric sealants
C-661-83	Test for indentation hardness of elastomeric type sealants by means of a Durometer
C-669-75 (reapproved 1981)	Specification for glazing compound for back bedding and face glazing of metal sash
C-679-71 (reapproved 1977)	Test for tack-free time of elastomeric type joint sealants
C-681-84	Test for volatility of oil and resin-based, knife-grade, channel glazing compounds
C-711-72 (reapproved 1983)	Test for low-temperature flexibility and tenacity of one-part elastomeric solvent-release type sealants
C-712-72 (reapproved 1983)	Test for bubbling of one-part elastomeric solvent-release type sealants
C-713-84	Test for slump of an oil base knife-grade channel glazing compound
C-717-84d	Definition of terms relating to building seals
C-718-72 (reapproved 1983)	Test for UV cold box exposure of one-part elastomeric solvent-release type sealants
C-719-79	Test for adhesion and cohesion of elastomeric joint sealants under cyclic movement
C-731-82	Test for extrudability after package aging of latex sealing compounds
C-732-82	Test for aging effects of artificial weathering on latex sealing compounds
C-733-82	Test for volume shrinkage of latex sealant compounds
C-734-82	Test for low-temperature flexibility of latex sealing compounds after artificial weathering
C-736-82	Test for extension/recovery and adhesion of latex sealing compounds after artificial weathering
C-741-85	Test for accelerated aging of wood sash face glazing compound
C-742-73 (reapproved 1984)	Test for degree of set for wood sash glazing compound
C-765-73 (reapproved 1984)	Test for low temperature flexibility of preformed tape sealants

**Table 25. (Continued)**


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C-766-84	Test for adhesion after impact of preformed tape sealants
C-771-74 (reapproved 1980)	Test for weight loss after heat aging of preformed sealing tapes
C-772-74 (reapproved 1980)	Test for oil migration or plasticizer bleed-out of preformed sealing tapes
C-782-74 (reapproved 1980)	Test for softness of preformed sealing tapes
C-790-84	Practices for use of latex sealing compounds
C-792-75 (reapproved 1980)	Test for effects of heat aging on weight loss, cracking and chalking of elastomeric sealants
C-793-75 (reapproved 1980)	Test for effects of accelerated weathering on elastomeric joint sealants
C-794-80	Test for adhesion-in-peel of elastomeric joint sealants
C-797-75 (reapproved 1981)	Recommended practices and terminology for use of oil and resin based putty and glazing compounds
C-804-83	Standard practice for use of solvent-release type sealants
C-834-76 (reapproved 1981)	Specification for latex sealing compounds
C-836-84	Specification for high solids content, cold liquid-applied elastomeric waterproofing membrane for use with separate wearing course
C-879-78 (reapproved 1984)	Methods for testing release papers used with preformed tape sealants
C-898-84	Guide for use of high solids content, cold liquid-applied elastomeric waterproofing membrane with separate wearing course
C-907-79 (reapproved 1984)	Test for tensile adhesive strength of preformed tape sealants by disk method
C-908-84	Test for yield strength of preformed tape sealants
C-910-79 (reapproved 1985)	Standard test for bond and cohesion of one-part elastomeric solvent release type sealants
C-919-84	Practice for use of sealants in acoustical applications
C-920-79	Specification for elastomeric joint sealants
C-957-81	Specification for high solids content, cold liquid-applied elastomeric waterproofing membrane with integral wearing surface
C-961-8	Test for lap shear strength for hot applied sealing compounds
C-962-81	Guide for use of elastomeric joint sealants
C-972-82	Test for compression/recovery of tape sealants
C-981-83	Guide for design of built-up bituminous membrane waterproofing systems for building decks
C-1016-84	Test for determination of water absorption by sealant backup ( joint filler) material
C-1021-84	Practice for laboratories engaged in the testing of building sealants
C-2202-84	Test for slump of caulking compounds and sealants
C-2203-84	Test for staining of caulking compounds and sealants
C-2249-74 (reapproved 1984)	Predicting the effect of weathering on fact glazing and bedding compounds on metal sash
C-2376-84	Test for slump on face glazing and bedding compounds on metal sash
C-2377-84	Test for tack-free time of caulking compounds and sealants
C-2450-75 (reapproved 1981)	Test for bond of oil and resin-base caulking compounds
D-2451-75	Test for degree of set for glazing compounds on metal sash
D-2452-75 (reapproved 1981)	Test for extrudability of oil and resin-base caulking compounds
D-2453-75 (reapproved 1981)	Test for shrinkage and tenacity of oil and resin-base caulking compounds

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**Table 26. Sources of Specifications.****ASTM Specifications**

American Society for Testing and Materials  
1916 Race Street  
Philadelphia, PA 19103  
(215)299-5400

**AASHTO Specifications**

The American Association of State Highway and  
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# Pressure-Sensitive Adhesives for Tapes and Labels

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Pressure-sensitive adhesives (PSAs) are materials which in dry form are aggressively and permanently tacky at room temperature and firmly adhere to a variety of dissimilar surfaces upon mere contact without the need of more than finger or hand pressure.<sup>1</sup> They are widely used in familiar, everyday products such as masking tapes and office tapes, finger bandages and labels.

The true PSA does not require activation by solvents or heat and adheres firmly to a wide variety of surfaces. Despite their aggressive tackiness, "they can be handled with the fingers and removed from smooth surfaces without leaving a residue."<sup>1</sup>

The earliest commercial PSAs of importance were blends of natural rubber (NR) and wood rosin.<sup>2</sup> The rosin, subsequently categorized as a member of a class of materials called *tackifying resins*, imparted to the rubber the necessary degree of tackiness. With the NR/rosin blends, largely in response to a need for masking parts to be protected in painting operations, the PSA industry had its origins. In time other elastomers were utilized and the original wood rosin was chemically modified to provide a large variety of tackifiers. Hydrocarbon-based tackifiers were added and other elastomeric polymers, particularly polyacrylates, came into use after World War II.

The availability of PSAs with improved

properties led to an explosive growth in their use. From a post-World War II value of less than \$100 million the industry has expanded to a current dollar volume, at the manufacturer's level, of about \$3 billion.<sup>3</sup> Tapes account for roughly 60% of this market, with labels, including decals, taking about 30%. The remainder is utilized for decorative and protective sheets, sanitary napkins, floor tiles, various medical applications, sun control films, EMI shielding and numerous specialty items. The PSA market additionally requires a significant dollar volume of release coatings, to provide surfaces to which the PSA has low adhesion for handling and transfer of products.

Originally PSA products were manufactured by drying a solution of the adhesive on a suitable backing. In the 1970s, in response to cost increases in solvents and regulatory restrictions regarding emissions, the industry turned to water-based (emulsion) PSAs and 100% solid compositions or so-called hot melt pressure-sensitive adhesives (HMPSAs). These market forces have had a profound effect on the selection of PSA materials.

Although rubber-based adhesives still constitute the largest component of the PSA market, NR has been supplanted by the styrene-isoprene-styrene (S-I-S) block copolymers as the dominant hydrocarbon elastomer in this category because, to a large extent, the S-I-S

polymers lend themselves to hot melt formulations; in contrast, NR adhesives are still mostly solvent-based. The utilization of latex vehicles based on hydrocarbon elastomers is still relatively minor and is largely restricted to styrene-butadiene emulsions and some natural rubber latex. However, in the case of acrylic PSAs, emulsions now surpass solution adhesives in volume consumed.

These trends are expected to continue, with water-based and hot melt formulations gradually supplanting solution polymers. A newer technology, radiation polymerization or cure of PSAs, at present is of minor industrial importance, although at least two of the major producers of PSA products are reported to operate manufacturing lines utilizing electron beam radiation. UV radiation use may grow in time.

## CONSTRUCTIONS

Pressure-sensitive products basically consist of an adhesive coated on a backing or carrier. Most often the backing is a flexible film, foil, or fabric, although many products utilize rigid supports or have the adhesive directly coated onto the form or object that is to be bonded to another surface. A typical construction is shown in Fig. 1.

### Manufacture

PSAs are applied to backings in several ways depending on the nature of the adhesive. Solutions or latices are coated on a moving web of backing or release liner, in a continuous operation including drying in an oven. If the adhesive is coated on a release paper or liner, it can be subsequently laminated or transferred to the desired backing and the liner retained or removed. Hot melts, or 100% solid adhesives,

are applied to the backing using either a hot melt coater, a calendar, or an extruder. For most purposes the final coating is relatively thin, of the order of 2–3 mils in thickness, but it may be as thick as 12 mils. In general, the 100% solids adhesive lend themselves better than solutions or latices to heavier coatings.

**Drying Lines.** Oven drying lines represent large capital investments, of the order of several million dollars, and the same line is frequently used to handle both solutions and latices. The metering equipment may be either reverse roll coaters, which offer maximum flexibility, or knife-over-roll coaters, which are less expensive. For thin films a wire-wound rod to remove excess material can be used. Because of coating difficulties encountered with latex vehicles such devices as an air knife or flexible blade are sometimes used with these products.

Coating of tapes is often directly onto the backing. Label adhesives, in contrast, are always coated on a release liner which is then laminated (nip rolls) to the paper or other backing and used or sold in this construction.

The drying step of necessity must be relatively slow to avoid bubbles, etc., and the web speed in commercial ovens is usually restricted to 25–50 yards per minute. Hot air ovens are the most common type of dryer, although the air flow is often supplemented by infrared heating. For solvent operations the modern oven either incinerates the solvents, for fuel value, or permits recovery of the solvent by condensation or by absorption on activated charcoal.<sup>4</sup> The energy requirements for drying latices are actually less than for solvents since less hot air is required; the air volume must be large to avoid an explosive concentration of vapors in the case of solvents.

In almost all cases the adhesive is coated on wide-width material and then slit into narrow widths for tapes, which are subsequently wound into rolls, or diced or otherwise cut into the shapes desired for other products.

**Hot Melt Coating.** HMPSAs are heated to achieve a bulk viscosity suitable for the equipment used and then conveyed to a roll-backed web. The term *hot melt coater* refers to equipment that has viscosity limitation, while an *ex-*

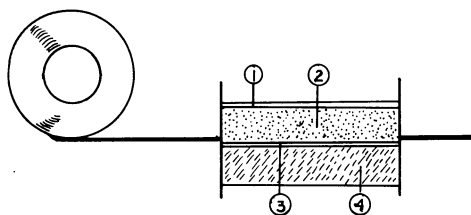


Fig. 1. PSA tape construction. 1, release coating; 2, backing; 3, primer; 4, adhesive.

*truder* can handle materials of quite high viscosity. Accordingly the adhesives suitable for hot melt coating are restricted in molecular weight. The most popular machines pump the molten polymer from a reservoir through a slot die, although other devices are also used.

Extrusion coating, although currently practiced only by a few large PSA manufacturers, appears to be of growing importance because it permits utilization of high molecular weight compositions. For rubber-based adhesives the equipment provides for in-line mixing of rubber and tackifier. For acrylic adhesives twin-screw extruders can devolatilize solutions or emulsions and deliver 100% solids through the slot die. Both hot melt coater and extruders are capable of delivering over 1000 pounds an hour of adhesive.

Hot melt machines require a much smaller capital investment than extruders, and narrow width coaters are used by label manufacturers and for smaller scale tape operations. Extruders are justified only in the case of a single large-volume product.

**Calendering.** This older technique, highly capital intensive, is of declining importance for PSAs. Because it is still a preferred process for thick coatings, calendering is used for pipe wraps, where the adhesive thickness may be as much as 12 mils. Calendering is also used for making fabric-backed duct tapes, where heavy applications are required to compensate for the adhesive buried in the backing, but it is doubtful if new production of PSAs will utilize calenders.

### Backings

Because of the myriad applications found for PSA products, a large number of backing materials or carriers are needed to satisfy end-use requirements. For tapes and labels thin and flexible materials such as paper, films, fabrics, and foils constitute the major share of backings. For other products, such as floor tiles or name plates, the backing can be rigid and thick. Other backings, for example Velcro strips, can be intermediate in rigidity.

Paper is the most widely used backing and, in fact, constitutes about 80% of the label mar-

ket on an area basis. At the thickness most commonly used, about 5–6 mils, paper is much less expensive than films but subject to delamination. Accordingly, for tape purposes the paper is strengthened by impregnation with a polymeric saturant such as a styrene-butadiene or acrylic latex. Often the paper is creped to enhance its conformability to rough surfaces. Paper tapes are used for masking, packaging, electrical insulation, identification and splicing, with masking tape for the automotive industry taking the largest volume. In many applications, such as packaging, paper is being replaced by films, particularly polypropylene film. The paper backing used for labels is seldom latex-impregnated. A large amount is clay-coated to permit better printing quality.

Film backings are stronger than paper per unit thickness and offer additional advantages including transparency and water resistance. Cellophane was the first film used for a PSA product but has now been replaced by cellulose acetate for transparent office and household tape. Oriented polypropylene is used in enormous volumes, approaching that of paper, for diaper tapes, strapping tapes, and other packaging applications. Other widely used films are polyester, for electrical and packaging applications as well as decorative sheets, and polyvinyl chloride for electrician's tape, fingerbandages, medical products, decorative sheets and labels. Polyethylene is little used except as thick films for corrosion protection tapes for underground transmission pipes. Among the lesser used films are those of nylon, polyimide, metallized polyester, fluorocarbon, and polyurethane—all of which fit some special niche in the market place.

Many films are reinforced with fibers or laminated to fabric, an important segment of the duct tape market, and metal for nameplates.

Fabric or cloth backings are used for medical tapes, finger bandages and electrical tapes. Other specialty backings include metal foils and foams.

### Release Coatings and Liners

Release coatings are an essential feature of PSA technology. Self-wound tapes often require an adherent or antistick coating on the reverse side

of the backing to permit facile unwind of a roll. Labels and many specialty products are always backed with an antistick or release-coated liner; some tapes are also wound with a release interliner. The release liner is most often coated with a polymeric material of low surface energy or composed of a film, also of low surface energy, to which the PSA adheres poorly. Note that if the backing does not have good adhesion to the PSA but is primed or chemically altered to provide good anchorage of the adhesive, then no release coating is required.

The release coating, applied as a very thin film to the reverse side of the backing (see Fig. 1), can be a silicone or an alkyd or copolymer containing long aliphatic hydrocarbon constituents. Thus, ethylene *bis*-stearamide, for example, can be added to a paint vehicle or, less commonly, used alone. The copolymers are crosslinkable emulsions of an acrylate or vinyl acetate containing a monomer like stearyl acrylate. Other polymers or materials that provide a low energy hydrocarbon moiety, which tends to concentrate in the surface, are used to a lesser extent.

Silicone coatings represent about one-quarter of tape release coatings (in area) but completely dominate the release liner field. The most common liner substrate is kraft paper or, to a limited extent, polyethylene-coated paper. Silicone vehicles may be either solutions (by far the most common), or emulsions of self-crosslinking poly(dimethylsiloxane) polymers which are coated and oven dried in a continuous operation. Solventless or 100% solids coatings have also been developed. Electron beam cured coatings, also solventless, may be accepted in the future but at present represent a very small part of the market. In-house production of release liners is conducted by many PSA tape and label manufacturers but most purchase liner stock from paper companies.

## ADHESIVE SYSTEMS

Natural rubber, a hydrocarbon elastomer, was the first material utilized in making PSAs and is still widely used today. The term *rubber-based* now includes many new synthetic elastomers as well as natural rubber (NR). With all rubber-based PSAs an essential ingredient is a

tackifier, which normally constitutes 35–50% by weight of the adhesive. These tack-enhancing materials are also used with other types of elastomer and thus constitute an important, and even essential, raw material in formulating PSAs.

## Tackifiers

Tackifiers were originally produced from the rosin found in wood. The wood rosins derived from aged tree stumps, or *naval stores*, contain various unsaturated acids, e.g., abietic and levopimaric, as a major constituent. To obtain more aging stability and compatibility with base polymers, these acids have been modified by hydrogenation, disproportionation, and esterification (Fig. 2) with glycerol or pentaerythritol; little unmodified rosin is used today. Partially hydrogenated rosin esters are increasingly utilized.

Wood turpentine, also from tree stumps, is the source of another important group of tackifiers. Cationic polymerization of dipentene and  $\alpha$ - and  $\beta$ -pinene, the major constituents of turpentine, yields the terpene tackifiers (Fig. 3).

Tall oil, a byproduct of the paper industry, has now surpassed naval stores as a rosin

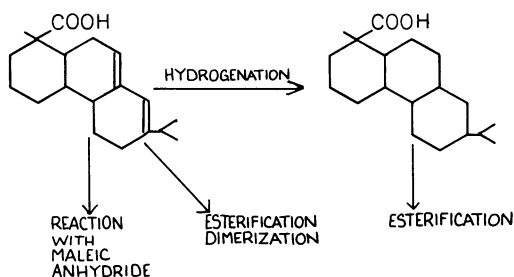


Fig. 2. Chemistry of rosin ester tackifiers. Rosin actually contains other components besides abietic acid.

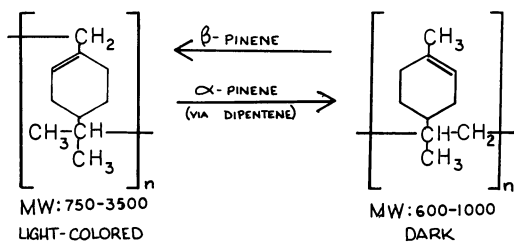


Fig. 3. Chemistry of polyterpene tackifiers.

source. The tall oil rosins are very similar to the wood rosins and similarly modified.

Lower cost tackifiers, derived from oligomerization of unsaturated petroleum fractions, are now the most heavily used for PSA manufacture. Both the  $C_5$  and the  $C_9$  fractions are utilized; the former has greater industrial importance on the basis of broader compatibility with PSA base polymers.

Tackifiers with aromatic content, particularly  $\alpha$ -methyl styrene and vinyl toluene copolymers and coumarone-indene resins, are of significant industrial value.

Tackifiers are all low molecular weight materials, ranging from about 300 to about 3000. Some are liquids but the most widely used tackifiers are brittle solids having ring and ball softening points of about 60–115°C. For most effective behavior the tackifier should be close in solubility parameter to the elastomer with which it is blended.<sup>5</sup> Thus aliphatic hydrocarbon tackifiers are not indicated for use with the polar acrylic PSAs.

For use with latex adhesives, the tackifiers are produced as aqueous dispersions. It is important here that the dispersants used be compatible with the surfactant in the polymer emulsions.

## Rubber-Based Adhesives

**Natural Rubber.** Natural rubber (NR), all *cis*-1,4-polyisoprene, is available as the natural latex, but the major raw material for PSAs is the recovered solid, or baled gum rubber. The principal types of NR used for PSAs are pale crepe or ribbed smoked sheet, which is less expensive but of darker color. The baled rubber must be masticated to lower its molecular weight before use.

Most NR-based adhesives are sold as solutions, usually about 35% solids, in  $C_6$ – $C_7$  aliphatic hydrocarbons, often blended with some toluene. With this elastomer almost any tackifier can be used, but terpenes and  $C_5$  hydrocarbon types are favored. Tack (see below) reaches a maximum at 50–70 parts tackifier per 100 parts (phr) NR, depending on the tackifier. Often a mixture of tackifiers gives better properties. The PSA composition often includes fillers such as clay to lower costs and alter

properties, and plasticizers such as petroleum oil or low MW polyisobutylene. Antioxidants are always added to protect the unsaturated backbone from oxidative degradation. Some typical formulations are given in Table 1.

NR latex is used for PSAs to a small extent. Here the tackifier must be in the form of an aqueous dispersion.

Synthetic polyisoprene, chemically similar to NR, has the advantage of not requiring milling like NR in order to prepare solutions. Nevertheless, its use in PSAs is about one-tenth that of NR because of costs and poorer cohesive strength than NR. For these reasons and because of competition from other elastomers, its usage is not expected to grow.

**Block Copolymers.** The hydrocarbon elastomer enjoying the greatest volume in PSAs is an A-B-A triblock copolymer where A is polystyrene and B is either a polyisoprene or polybutadiene unit. These polymers are trademarked "Kraton" by Shell Chemical Com-

**Table 1. Typical PSA Formulations Based on NR.**

<b>A. General Purpose: Clear</b>	
Milled pale crepe	100
Polyterpene (MW 750)	90
Antioxidant	2
Heptane	350
<b>B. General Purpose: Pigmented</b>	
Milled pale crepe	34
$C_5$ hydrocarbon resin (s.p. 95°C)	34
Dixie clay	20
Titanium dioxide	11
Antioxidant	1
(Can be calendered)	
<b>C. Surgical Tape</b>	
Milled smoked sheet	100
Rosin ester (s.p. 95°C)	90
Lanolin	20
Zinc oxide	50
Antioxidant	2
(Solvent to coatable viscosity)	
<b>D. Masking Tape</b>	
Milled pale crepe	100
Polyterpene (s.p. 115°C)	41
Calcium carbonate	58
Resole phenolic	51
Antioxidant	2
Hexane/toluene (70/30)	450

pany, the only domestic producer. By far the more popular copolymer is that in which the midblock is composed of isoprene units; this material yields adhesives of higher tack than those with butadiene midblocks. The copolymers have an overall molecular weight of about 100,000 with about 15–30% by weight of polystyrene.<sup>6</sup>

These triblock copolymers develop a domain structure; the polystyrene blocks from various polymers aggregate into domains which function as thermolabile crosslinks. On heating above the glass transition temperature  $T_g$  of the amorphous polystyrene end units, the material behaves as a typical thermoplastic and may be pumped or extruded. On cooling, the polystyrene domains reform and the copolymer behaves like a crosslinked rubber. Similarly, the copolymer may be dissolved like a thermoplastic and on evaporation of the solvent regain the domain morphology and behave again as if crosslinked. The thermolability of the “crosslinks” permit formulation of the Kraton as HMPSAs. Currently, the triblock-based adhesives make up almost 100% of the HMPSA market.

Block copolymers are also widely used in the form of solution adhesives. Although higher cost than NR, their low MW permits making higher solids content solutions which have obvious economic and ecological advantages.

Hydrogenation of the diolefinic midblock of a S-B-S copolymer gives an elastomer, designated Kraton G, which is favored for HMPSA applications, in spite of lower tack than the S-I-S copolymer, because of greater resistance to oxidative breakdown. Since poly(isoprene) degrades primarily by chain scission while poly(butadiene) tends to crosslink, mixtures of S-I-S and S-B-S polymers are sometimes used to minimize the effects of degradation.

A similar block copolymer targeted for the hot melt market has recently been introduced by Firestone. This product, Stereon 840A, is a multiblock styrene-butadiene copolymer. It has a higher styrene content and somewhat lower MW than the Kratons. A typical PSA formulation using Stereon is given in Table 2.

The tackification of the triblock copolymers differs from that of other elastomers in that two tackifiers, of quite different solubility param-

**Table 2. Typical PSA Formulation Using Stereon 840A.**

Stereon 840A	47.0
Hydrogenated rosin ester (s.p. 100°C)	31.5
Naphthenic oil	30.0
Antioxidant	1.5

ter  $\delta$ , are often used. One tackifier, with  $\delta$  below 9, is compatible with the midblock while the other,  $\delta$  above 9, is compatible with the high- $T_g$  end blocks. Midblock tackifiers are mostly  $C_5$  hydrocarbon resins and terpenes. The endblock tackifiers, such as  $\alpha$ -methylstyrene polymers or coumarone-indene resins, are of high  $T_g$  and reinforce or stiffen the polystyrene domains. Oils, included in many formulations to lower the melt viscosity, can have little aromatic character to avoid entering and softening the polystyrene domains. Typical formulations using Kraton block copolymers are given in Table 3.

#### Styrene-Butadiene Random Copolymers.

The SBR preferred for PSA usage differs from the SBR used primarily as an elastomer. The former is emulsion polymerized at a higher temperature and thus has a broader molecular weight distribution and a gel fraction, both attributes having advantages for PSAs. The consumption of SBR in this field is now about the same as that of NR.

**Table 3. PSA Formulations Based on S-I-S Block Copolymers.**

<b>A. Solution Formulation</b>	
Block copolymer (Kraton 1107)	100
Hydrogenated rosin ester (s.p. 104°C)	84
Liquid hydrogenated rosin ester	35
Antioxidant	1
Hexane/toluene (70/30)	180
<b>B. Hot Melt</b>	
Block copolymer	100
$C_5$ hydrocarbon resin (s.p. 95°C)	100
Naphthenic oil	40
Antioxidant	2
<b>C. Higher Shear Hot Melt</b>	
Block copolymer	100
$C_5$ hydrocarbon resin (s.p. 95°C)	100
Coumarone-indene resin (s.p. 155°C)	60
Naphthenic oil	40
Antioxidant	4

Most of the SBR used in PSAs is obtained as gum rubber and compounded as solvent adhesives. The major utilization is in label manufacture. Preferred tackifiers are rosin esters and  $\beta$ -pinene resins; the  $C_5$  hydrocarbon resins are not used. Typical solution formulations are shown in Table 4.

Recently SBR latexes have been promoted for PSAs but the higher cost of tackifier dispersions and the competition of the more oxidatively stable acrylic PSAs have limited their growth. What SBR latex is used is found mainly in the label and decal area.

**Polyisobutylene and Butyl Rubber.** The homopolymer of isobutylene, PIB, available commercially in a wide range of MWs, has the advantages of a saturated backbone and low permeability to water and gases. PSA compositions consist of a high MW polymer,  $M_v$  of from 725,000 to over 2,000,000, blended with a low MW PIB which functions as a plasticizer as well as providing a portion of low MW chains to promote wet-out of surfaces to which the adhesive is applied. The preferred tackifiers are  $C_5$  hydrocarbon resins and polyterpenes. Because PIB is a low energy polymer, for adhesion to more polar surfaces, rosin esters can be used. Most PIB adhesives are solvent based, with petroleum fractions (naphthas) being suitable solvents. A major use of PIB

**Table 5. PSA Formulations Based on PIB.**

<b>A. Removable Label</b>	
PIB (MW 2 million)	100
Polybutene (MW 1200)	70
Liquid hydrogenated rosin ester	35
$C_5$ hydrocarbon resin (s.p. 100°C)	45
Antioxidant	1
Heptane	1000
<b>B. Medical Tape</b>	
PIB (MW > 1 million)	100
PIB (MW 55,000)	30
Zinc oxide	50
Hydrated alumina	50
USP white oil	40
Phenolic resole	50
Antioxidant	1
(Solvent to coatable viscosity)	
<b>C. Vinyl Floor Tile</b>	
Butyl rubber (MW 450,000)	100
PIB	20
Terpene phenolic resin	70
Mineral spirits	360

PSAs is for removable labels, where low tack and adhesion are desirable. Typical formulations containing PIB are given in Table 5.

Butyl rubber is a copolymer of isobutylene with a minor amount of isoprene (0.8–2 mole %). Unlike PIB, butyl can be crosslinked to improve the otherwise poor cohesive properties of this class of adhesive. The major use for BR is in anticorrosion wrap for gas and oil transmission pipes. The backing for this tape consists of a thick polyethylene or PVC film, loaded with carbon black. The adhesive mass, which is quite thick (up to 12 mils) not only contains the usual tackifiers, of which many can be used, but also a high concentration of particulate filler. This tape lends itself favorably to calendar manufacture. A typical formulation for a pipewrap adhesive is given in Table 6.

**Table 4. PSA Solution Formulations Based on SBR.**

<b>A. General Purpose Tape</b>	
SBR	100
Hydrogenated rosin ester (s.p. 104°C)	75
Antioxidant	2
Toluene	180
<b>B. Removable Label Stock</b>	
SBR (54 Mooney Viscosity)	100
Hydrogenated rosin ester (s.p. 105°C)	50
Plasticizing oil	37
Antioxidant	2
Toluene	200
<b>C. Masking Tape</b>	
SBR (54 Mooney Viscosity)	100
$C_9$ hydrocarbon resin	150
Bromomethyl phenolic resole	20
Zinc resinate	5
Antioxidant	2
Hexane/toluene (60/40)	275

**Table 6. Typical Formulation for Calenderable Pipewrap Adhesive.**

Butyl rubber (MW 350,000)	100
Polybutene (MW 900)	100
Carbon black	90
Talc or clay	200
Process oil	50
$C_5$ hydrocarbon resin (s.p. 105°C)	75
Amorphous polypropylene	50

**Reclaim Rubber.** Rubber recovered from scrap rubber goods, primarily by digestion or mastication at elevated temperatures, consists of soluble hydrocarbon, crosslinked rubber, and about 30% carbon black, plus minor amounts of oil, tackifiers, and curative residues. The rubber content of reclaim derived from tires is a mixture of SBR and NR, while butyl reclaim is derived from inner tubes. One of the principal virtues of reclaim is price. It is used for black friction tape but to a larger extent for duct tapes and pipewrap tapes.

#### Ethylene-Vinyl Acetate Copolymers.

EVA copolymers having a vinyl acetate content of 40% or higher have some utility in PSAs. These copolymers, which also require high levels of tackifiers, were at one time the base materials for HMPSAs but have been almost completely displaced by the triblock copolymers. Although somewhat lower in cost than styrenic block copolymers, EVA has been unable to compete successfully because of low tack and poor shear strength, especially at elevated temperatures.

#### Acrylics

Poly(acrylate esters), often called acrylics, have grown from their first introduction in the mid-1950s to account for about one-quarter of the domestic PSA market. The pioneering research in this field by Ulrich<sup>7</sup> revealed that the normally tacky polymers of certain acrylic esters could be converted to useful adhesives by the incorporation of up to about 10% of a polar monomer. The acrylate esters of  $C_4$ – $C_{12}$  alcohols, giving homopolymers having a  $T_g$  of about  $-50^\circ\text{C}$  to about  $-75^\circ\text{C}$ , are the major constituent of the PSA.

For economic reasons the dominant esters worldwide are butyl and 2-ethylhexyl acrylate. The 3M Company, the largest tape producer in the U.S., is reported to manufacture for captive consumption the ester of isooctyl alcohol derived from the OXO process. Other acrylate esters, such as decyl and isodecyl acrylate, and certain methacrylate esters, such as lauryl methacrylate, give rise to the requisite low- $T_g$  homopolymer but are currently too expensive for commercial consumption. Although a large

number of comonomers have been mentioned in patents, acrylic acid is the most popular polar comonomer; others, such as acrylamide, acrylonitrile, hydroxyethyl acrylate, and certain amine-functional monomers, have found commercial utilization.

A so-called modifying monomer, such as vinyl acetate or ethyl acrylate, is very frequently included in acrylic PSA compositions to increase the  $T_g$  (see the Theory section, below). Typical recipes for acrylic PSAs are given in Table 7.

Acrylics, by virtue of their saturated backbone, far surpass the rubber-based PSAs in terms of aging stability. The acrylics are also colorless and can be readily tailored to suit specific applications by adjustment of the monomer ratios. As a generalization, acrylics adhere better to polar surfaces than rubber-based PSAs but, correspondingly, less well to low energy surfaces.<sup>8</sup> Although acrylic PSAs do not discolor or lose adhesive properties on outdoor exposure, their tack and peel strength, again as a

**Table 7. Typical Compositions of Acrylic PSAs.**

<b>A. General Purpose Tape</b>	
2-Ethylhexyl acrylate	75
Vinyl acetate	20
Acrylic acid	4
N-Methylolacrylamide	1
<b>B. Conformable, High Tack Adhesive</b>	
Isooctyl acrylate	95.5
Acrylic acid	4.5
Hydrogenated rosin ester (s.p. $85^\circ\text{C}$ )	50.0
<b>C. Firm, Repositionable Adhesive</b>	
Isooctyl acrylate	57.5
Methyl acrylate	37.0
Acrylic acid	7.5
<b>D. Self-Crosslinkable Adhesive</b>	
2-Ethylhexyl acrylate	89.5
Dimethylaminoethyl methacrylate	7.0
Acrylic acid	3.0
Glycidyl methacrylate	0.5
<b>E. Post-Crosslinkable Adhesive</b>	
2-Ethylhexyl acrylate	72.5
Vinyl acetate	18.9
Ethyl acrylate	5.2
Maleic anhydride	3.4
Add 0.3 metal alkoxide or acetylacetonate to coating solution	



generalization, are somewhat less than that of the best rubber-based adhesives. Another significant difference is that acrylics do not require tackification to provide excellent physical properties. Nevertheless, many commercial acrylic PSAs contain tackifiers, most often rosin esters, to increase peel adhesion and tack. Because acrylics can be free of antioxidants and tackifiers, they are generally regarded as less irritating to the skin and are often preferred for medical applications.<sup>9</sup>

Although the acrylics were originally available only as solution adhesives, the rising cost of solvents and the amendments to the Clean Air Act in the 1970s created strong motivation for water-based forms. Today acrylic emulsions volume exceeds that of acrylic solutions, and the trend toward the emulsions is expected to accelerate in the future. Once offered commercially,<sup>10</sup> hot melt acrylic PSAs are no longer on the market except for a minuscule amount of HMPSA material designed for post-radiation curing. It has been extremely difficult to develop compositions with adequate shear strength at the low molecular weights required for hot melts.

Solution adhesives are limited in MW because of the effect of MW in increasing solution viscosity. In contrast, since MW of the polymer has no effect on latex viscosity, this factor does not operate with latex adhesives. Often, however, some chain transfer agent is incorporated in the emulsion recipe to lower MW of the polymer in order to obtain better tack. To compensate for the low MW of solution adhesives, it is common practice to effect crosslinking of the dried adhesive in the oven drying line. Melamine resins are used<sup>11</sup> as well as the soluble derivative of a multifunctional metal, e.g., aluminum acetyl acetate<sup>12</sup> or a titanium alkoxide,<sup>13</sup> which loses its ligand and effects salt crosslinks with the carboxyls in the polymer on drying. Some latex polymers are also crosslinked e.g., by incorporating something like zinc acetate. Of increasing importance are the self-curing compositions where the crosslinking mechanism is built into the polymer.<sup>14,15</sup>

A new approach to achieving augmented cohesive strength without crosslinking is based on a polymer with pendant high- $T_g$  chains. The in-

compatible pendant chain forms domains in a manner analogous to the morphology generated in S-I-S copolymers. One method to provide the requisite pendant chain consists of grafting of, for example, styrene or methyl methacrylate to a preformed conventional acrylic polymer.<sup>16</sup> Another method involves copolymerization of a monomer, that is, a low MW polystyrene chain terminated with a methacryl group. A recently introduced product is Arco Chemical Co.'s Chemlink 4500 Macromer monomer, which, when copolymerized with an acrylate ester and a polar monomer, provides pendant chains of polystyrene.<sup>17</sup> Typical formulations using this macromer are given in Table 8.

Acrylic PSAs are used for some labels and a wide variety of tapes, particularly transparent office, strapping, transfer, medical, and metal foil tapes.

### Silicones

The use of silicone-type PSAs is restricted because of their high cost, in spite of the excellent adhesion to surfaces of both high and low surface energy and the ability to function acceptably at a temperature range of over 500°C. The base raw materials for producing silicone PSAs come primarily from Dow Corning and General Electric Corp.

The two basic components of a silicone PSA are a resin and a gum, somewhat analogous to tackifier and elastomer in organic adhesives. The resin is derived from reaction of silicic or polysilicic acid (hydrosol) with something like trimethyl chlorosilane to convert part of the OH

**Table 8. Typical PSA Formulations Using Macromer.**

<b>A. Untackified</b>	
Chemlink 4500 <sup>a</sup>	15
2-Ethylhexyl acrylate	80
Acrylic acid	5
<b>B. Tackified</b>	
Chemlink 4500 <sup>a</sup>	15
1-Decyl acrylate	82.9
Acrylic acid	2.1
Hydrogenated rosin ester (s.p. 85°C)	97.0
Trioctyl trimellitate (plasticizer)	16

<sup>a</sup>Arco Chemical Co.

groups to trimethylsiloxane groups. The concentration of residual Si—OH groups is less important than the MW of the resin, which is preferably less than 5000. The gum is a high MW polysiloxane with terminal OH groups. Both all-dimethyl and dimethyl-diphenyl polysiloxanes are used. The inclusion of diphenyl siloxane units, normally 6 or 12 mole percent of the gum, results in higher tack and peel adhesion in the resulting PSA. The simplest method of PSA preparation is mixing resin and gum in a suitable solvent, typically toluene. The solution can be used for coating as is, or heated to induce more Si—O—S formation, both intra- and intermolecular, which gives a product with higher cohesive strength. The physical properties of the PSA are a function of resin/gum ratio, type of gum, and amount of heating given the blend prior to coating. The effect of the resin/gum ratio, using an all dimethyl gum, is illustrated in Fig. 4.<sup>18</sup> An adhesive based on a partial diphenyl gum would have higher tack and peel adhesion values.

Silicone PSAs find application almost exclusively in tape form. Polyester film is widely used as backing particularly for masked printed circuit boards during plating operations, for electrical insulation and paper splicing tapes. Glass cloth-backed tapes are preferred for

masking and insulation where high temperatures are encountered. Special high performance silicone tapes include those with polyimide and poly(tetrafluoroethylene) as backings.

### Miscellaneous Polymers

Other than the hydrocarbon elastomers and acrylics, and to a smaller degree silicones, little success commercially has attended efforts to utilize other polymers for PSAs. The patent literature describes a number of water solubles, suitably crosslinked, as the base ingredient for repulpable adhesives on paper backings used to splice rolls during papermaking operations.<sup>19,20</sup> The patent literature also reveals efforts to utilize polyurethanes,<sup>21</sup> polyurethane-acrylic hybrids,<sup>22</sup> ionomers,<sup>23</sup> and polyester block elastomers,<sup>24</sup> among others, but only repulpable adhesives have reached the marketplace. Two systems that have achieved mentionable commercial success are described below.

**Vinyl Acetate Copolymers.** Available only as emulsions for PSA applications, the use of vinyl acetate copolymers is still relatively small and confined almost entirely to permanent la-

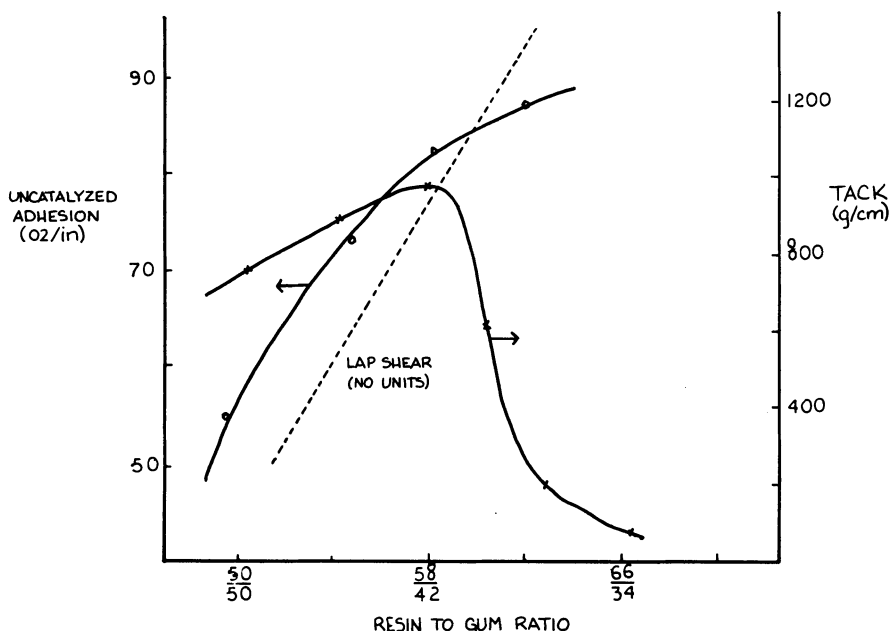


Fig. 4. Effect of resin-to-gum ratio in silicone adhesives on tack, adhesion and shear strength.<sup>18</sup>

bels. Some of the emulsions are used as such and some blended with an acrylic latex before application. Vinyl acetate copolymer adhesives are produced that have an excellent balance of tack, peel strength, and shear resistance; as with acrylics, adhesive strength builds with time. The only domestic producer, Air Products, does not reveal the composition of its PSAs but patents<sup>25</sup> indicate that they may be roughly 1:1 copolymers of vinyl acetate and dioctyl maleate containing some acrylic acid.

**Poly(Vinyl Alkyl Ether) Blends.** Vinyl ethyl ether polymers, available from Union Carbide and GAF, are used in medical products because of high moisture vapor permeability, valuable for patient comfort during long term application to the skin. Also of some small use are PSAs based on poly(vinyl isobutyl ether). The technology here involves blending high and low MW polymers, as illustrated in Table 9, analogous to the approach with PIB. Again, the low MW polymer provides for spreading on the adherend surface and the high MW polymer provides cohesive strength. The major drawback with this category of adhesive, not readily crosslinkable, is poor shear resistance.

## THEORY

The adhesive properties of PSAs, like other adhesives, are governed by two basic considerations, namely the ability to wet and spread on an adherend surface and the ability to resist detachment from that surface. Making a good bond is to a large extent, but certainly not entirely, dependent upon the relative surface en-

ergetics of the adhesive and adherend (basic to all adhesion phenomena), while resistance to debonding forces is, in the case of PSAs, a function of the viscoelastic behavior properties of the adhesive. Unlike structural adhesives, there is no phase change from liquid to rigid solid in the case of PSAs. Both surface energetics and especially viscoelastic properties are basic to the understanding of PSA behavior. In what follows there is a brief discussion of surface energetics but viscoelastic behavior is covered in the discussion of the three principal criteria by which PSAs are evaluated: tack, peel adhesion, and resistance to shear.

## Surface Energetics

In order to maximize bond strength between adhesive and adherend it is necessary that the liquid (adhesive) wet and spread over the solid to achieve close contact between the surfaces, that is, to eliminate voids or gaps at the interface. Although PSAs are fairly viscous at room temperature, experience shows that intimate contact, which means flowing into the pits and crevices of the solid surface (which is never microscopically flat) is obtained at short times under moderate pressure. Thus the ability of the PSA to flow into the asperities of the solid surface and achieve the desired intact interface is determined to a large extent by the relative surface energies of the two phases.

Surface tensions are readily determined for liquids, unlike solids. To ascribe surface energy values to solids, the concept of critical surface tension  $\gamma_c$ , as developed by Zisman,<sup>26</sup> is utilized. As a generalization, a liquid will spread on a surface which has a higher surface tension or free surface energy than that of the liquid.

These surface energies are the basis for calculating the thermodynamic work of adhesion,  $W_A$ , which also represents the work required to separate two surfaces. It must be stressed that  $W_A$  is far smaller than the force required to remove a PSA tape from a substrate; the experimental peel force includes significant contributions from the bulk viscoelastic properties of the adhesive and the backing, as pointed out later. Nevertheless  $W_A$  and peel force can be correlated.

**Table 9. PSA Formulations Based on Poly(Vinyl Alkyl Ether).**

A. Poly(Vinyl Isobutyl Ether) Type	
PVIBE MW 100,000	180
PVIBE MW 40,000	585
PVIBE MW 10,000	135
Antioxidant	5
B. Poly(Vinyl Ethyl Ether) Type	
PVEE Red. visc. 0.3	50
PVEE Red. visc. 4.0	25
Zinc resinate	5

$W_A$  can be expressed by two classical equations:

$$W_A = \gamma_s + \gamma_L - \gamma_{SL} \quad (1)$$

$$W_A = \gamma_L(1 + \cos \theta) \quad (2)$$

Where  $\theta$  is the contact angle,  $\gamma_{SL}$  is the interfacial surface tension and  $\gamma_s$  and  $\gamma_L$  are the surface energies or surface tensions (neglecting for simplicity that their measurement actually involves an interface with vapor) of solid and liquid, respectively. The first equation, applicable when the contact angle is zero ( $\gamma_L < \gamma_s$ ), emphasizes that adhesion increases to the point where  $\gamma_L$  is close to  $\gamma_s$  and then decreases. (When  $\gamma_s$  is greater than  $\gamma_L$ , the  $\gamma_{SL}$  will not be minimum.) It also reinforces the experimental observation<sup>27</sup> that  $\gamma_{SL}$  is the most important criterion of bond strength. The second equation (Young-Dupré), applicable when the contact angle is not zero, points out that as  $\theta$  approaches zero,  $W_A$  approaches  $2\gamma_L$ . This leads to the conclusion that for maximum  $W_A$ ,  $\gamma_L$  should be maximum, consistent with a low to zero contact angle.

Thus, based on thermodynamic considerations, maximum bond strength is approached when the adhesive has a surface energy close to but not exceeding that of the adherend. Although it is sometimes claimed that maximum adhesion for a particular adhesive increases continuously as the  $\gamma_c$  value of the substrate increases, this statement is only true when the  $\gamma_L$  of the liquid is higher than that of all the substrates involved. The predicted maximum in bond strength with increasing  $\gamma_c$  of the adherend has been observed experimentally by Toyama<sup>28</sup> in the case of PSAs, both rubber-based and acrylics. Toyama found  $\gamma_L$  for the adhesives to vary from 30 dynes/cm<sup>2</sup> for a PIB-based adhesive to about 36 dynes/cm<sup>2</sup> for a NR-based adhesive, a figure somewhat higher than that found by Dahlquist,<sup>29</sup> and a plot of peel force vs.  $\gamma_c$  for adherends showed a broad maximum at values of the adherends within 1 or 2 dynes/cm<sup>2</sup> of the PSA value.

The simplistic discussion above neglects the very important fact that surface energies are made up of contributions from both dispersion forces (roughly van der Waals forces) and polar

forces; the latter are probably not simply dipole-dipole interactions but are better ascribed to acid-base interactions.<sup>30</sup> The key point here is that interfacial tensions depend on polarity, that is, on the difference in polarity between adhesive and adherend; if only dispersion forces are operative,  $\gamma_{SL}$  is zero. Thus the effective energy of a solid surface really depends on the interactions possible with the liquid. This concept explains instances of specific adhesion, where an adhesive bonds more strongly to one surface than a second, both of which have equal  $\gamma_s$  or  $\gamma_c$  values but different polar components  $\gamma_s^P$  of that energy. Expressed another way, for optimum thermodynamic wettability, when the surface tensions of the two phases are similar, matching of the polarity of the two phases is very important.

On the basis of surface energetics it is understandable, not only that PSAs do not bond as well to solids of low  $\gamma_c$ , but also why the more polar acrylic PSAs bond better to polar surfaces like glass and rubber-based PSAs bond better to surfaces of lower polarity like polyolefins.

### Tack

To the layman the not clearly defined property of tack is often equated with stickiness and assessed by touching a PSA surface with a finger. ASTM defines tack as "the property of a material which enables it to form a bond of measurable strength immediately on contact with another surface."<sup>31</sup> The time of bond formation is thus a factor in tack, as is the force to unbond after contact, since the definition speaks of measurable strength. In other words, tack involves both a bonding and an unbonding force.

The quantitative value of tack will depend on the method of testing; the pressure used in making contact of the PSA with a surface, the time of contact, and the rapidity of removal all greatly influence the observed value. Note that the term *pressure-sensitive* arises because the strength of the bond is influenced by the contact pressure.

To effect a good bond immediately, that is, in short times of contact, the adhesive must not only have favorable surface energetics relative to that of the substrate, as discussed earlier, but

also a low viscosity and a low elastic modulus or high deformability.

Low viscosity need not be a characteristic of all the polymer in a PSA, but some fraction of the chains must be of sufficiently high mobility at the temperature of application to permit wetting the surface of the adherend in a short time. To function properly, therefore, the PSA must have a low  $T_g$  ( $-10^\circ\text{C}$  to  $-40^\circ\text{C}$  is typical), which implies high segmental jump frequency, and have a low enough viscosity to wet, which really means to spread over the adherend, in a short time.

Sheriff,<sup>32</sup> using rubber-tackifier blends over a range of concentrations, found that at low frequencies (using a Weissenberg rheogoniometer) both the in-phase shear modulus  $G'$  and the in-phase component of the dynamic viscosity  $\eta'$  of the elastomer were lowered as tackifier was added. At high frequencies, on the other hand, both  $G'$  and  $\eta'$  for the tackified blends were higher than that of the rubber, as illustrated schematically in Fig. 5. Lower frequencies are equivalent to longer times and bonding times, albeit short, are long compared to the times of peeling or unbonding. Accordingly, the lower viscosity and more compliant PSA

can make greater contact (enhanced wetting and spreading) with an adherent surface during the time defined by the tack test than can the untackified rubber. PSAs have viscosities in the range of  $10^6$ – $10^8$  poises at ambient temperature.<sup>33</sup>

The other component of tack, the force to unbond, is discussed more fully in the next section (Peel Adhesion) and emphasis in the consideration of tack is placed on the bonding process.

Tack can be related to modulus, as shown by Dahlquist<sup>34</sup> in an experiment in which tack and the complex tensile modulus  $E^*$  of a PSA were both measured as a function of temperature.  $E^*$  at 1 cycle/sec was found to drop with temperature until, at the temperature where the tack values become appreciable, it was below  $10^7$  dynes/cm<sup>2</sup>. At about  $35^\circ\text{C}$ , where tack was maximum, the modulus approached  $10^6$  dynes/cm<sup>2</sup>. Kraus<sup>35</sup> concluded, in work with tackified styrenic block copolymers, that to achieve satisfactory bonding the tensile storage modulus  $E'$  at 35 Hz must not exceed about  $10^7$  dynes/cm.

Bates<sup>36</sup> has developed a procedure to express tack as an energy term.

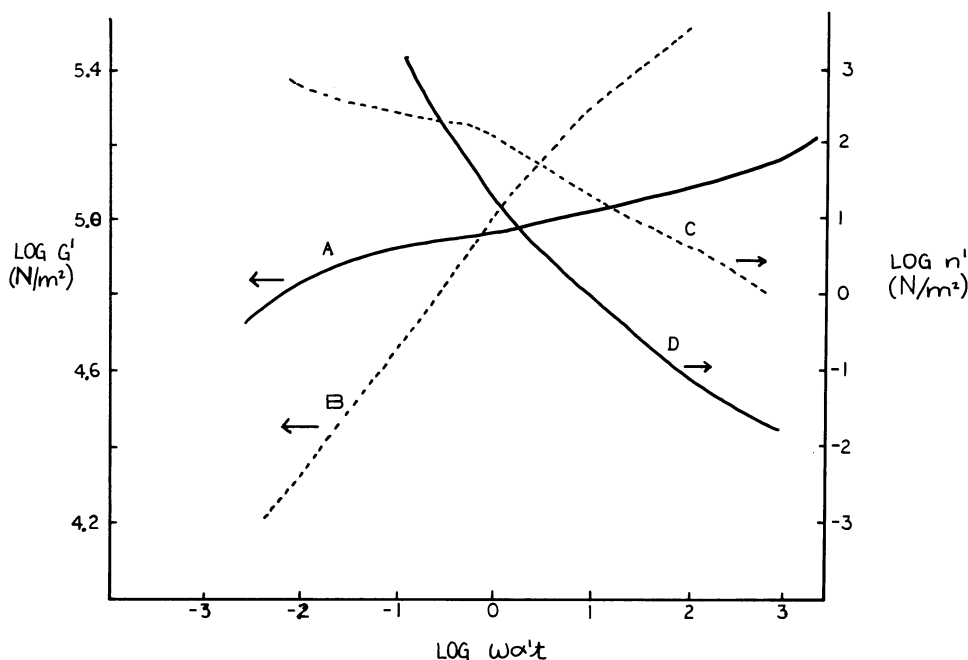


Fig. 5. Schematic master curves comparing in-phase shear modulus and dynamic viscosity with frequency of NR and tackified NR. A and D, natural rubber; B and C, natural rubber tackified with 50% hydrocarbon resin.

### Peel Adhesion

Quantification of peel adhesion involves measurement of the force required to remove the adhesive, obviously on some backing, from a specified surface at a specified rate of peel. Whereas in tack measurement the bonding and unbonding occurs within seconds of each other, adhesion tests are conducted after a specified but considerably longer dwell period of the adhesive on the test surface. Moreover, since significant pressure is used to enhance contact of the tape with that surface, there is the implication that a good bond has been achieved (although this obviously will not occur if the adhesive has a higher surface energy than the adherend or if the adhesive has low compliance and/or high viscosity), and the force required to unbond will be a measurement of the viscoelastic deformation of the adhesive. Many workers have indeed related peel adhesion to viscoelastic responses of the adhesive under the conditions of peeling.<sup>37-39</sup>

Plots of peel adhesion versus temperature,<sup>40</sup> Fig. 6, are almost inverse to the plots of peel adhesion versus rate of peel, shown schematically in Fig. 7. Both curves show a region where cohesive failure dominates, A in both

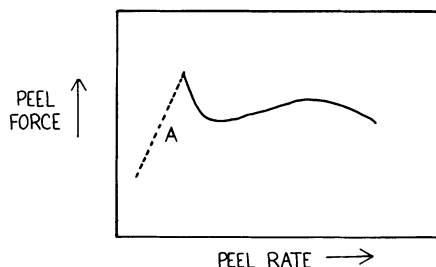


Fig. 7. Schematic plot showing effect of peel rate on peel force. A, region of cohesive failure.

figures, and a maximum in adhesion near the point where there is change to adhesive failure. It is evident that in the region of slow peel or high temperature, where the adhesive undergoes viscous deformation to split and leave a residue on the test surface, there is a different failure mode than in the high rate of peel or lower temperature region, where the adhesive exhibits a higher degree of elastic response or rubbery behavior and parts cleanly from the surface.

Using time-temperature superposition, and the shift factors of the WLF equation,<sup>40a</sup> it is possible to construct master curves relating pulling rate to peel force,<sup>41-43</sup> adjusted to some

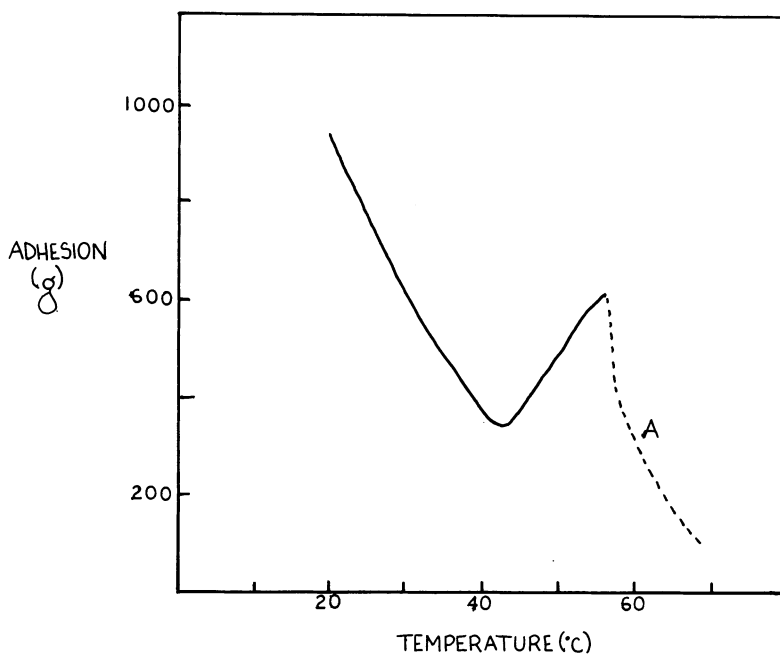


Fig. 6. Schematic plot showing effect of temperature on peel adhesion of PSA. A, region of cohesive failure.

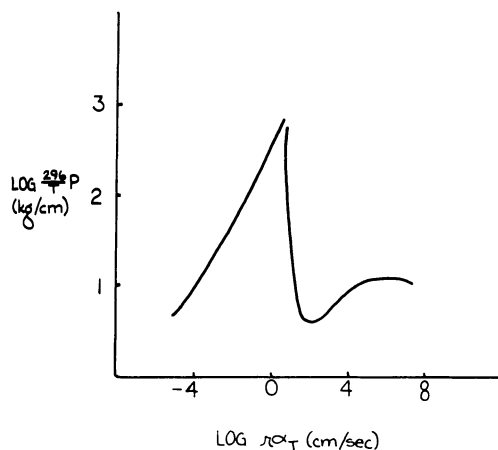


Fig. 8. Schematic master curve relating temperature and peel rate of a typical PSA in accordance with the WLF equation.

chosen temperature, usually 296°K. A typical master curve is shown in Fig. 8. A comparison by Aubrey and Sheriff<sup>44</sup> of curves of storage modulus  $G'$  and frequency of deformation with the peel force vs. peel rate curves, using NR-based adhesives, showed that the transition from viscous to rubbery behavior occurred at the same  $\log G'$  value regardless of the composition of the PSA. As noted below, increasing the  $T_g$  of the adhesive results in a shift of the master curve to the left along the frequency axis.<sup>45</sup> This study confirms that peel force is dependent on the viscoelastic state of the adhesive; a characteristic of simple viscoelastic materials is that their moduli increase with increasing rate of deformation.

An objective in the formulation of commercial PSAs is to achieve a peel force at ambient temperatures near the inflection point between viscous and rubbery behavior, but on the rubbery (clean interfacial separation) side, at a peel rate close to that used in the standardized tests.

Since the transition from viscous to rubbery behavior occurs near the glass transition temperature, it is evident that the point on the peel force versus peel rate curve at which there is a change from cohesive to interfacial separation will depend on the  $T_g$  of the adhesive. For practical purposes it is desirable to formulate the PSA to have a  $T_g$  that will yield a maximum in rubbery or clean peel at the test method rate of pulling. For NR-tackifier blends, the target  $T_g$

is attained at about 40% by weight of tackifier.<sup>45</sup>

### Cohesive Strength

The internal strength of the adhesive mass or its resistance to flow or creep under an applied load is referred to as the *cohesive strength*. PSTC defines cohesive strength as "the ability of the adhesive to resist splitting;"<sup>46</sup> upon deformation, the extended fibrils of a PSA<sup>47</sup> with low cohesive strength will rupture (split), leading to a residue on the adherend surface.

Cohesive strength can be equated with shear resistance and is most frequently assessed by a holding power test, that is, the measurement of the time for a tape to creep a specified distance or to fall from a test panel when a static load is applied in the plane of the backing (see Test Methods). The shear resistance of the amorphous polymer is thus a function of the viscous component of its viscoelastic response to the shear force and can be shown to be related to the steady-state flow viscosity.<sup>48</sup>

To limit the viscous flow of a PSA, that is, to increase its cohesive strength, it is necessary to increase the molecular weight and consequent chain entanglement contributions or to provide some crosslinking. (The obvious exception to this generalization occurs in the case of the domain polymers.) The increase in MW or the extent of crosslinking permissible in PSAs is limited by the need, as pointed out earlier, for the polymer to have a high compliance during the bonding stage. In the absence of crosslinking some portion of the polymer must possess very high MW (over 1 million) to minimize flow, while some portion must consist of material that must have short-time compliance. In the case of crosslinking it is found that a gel fraction concentration of 30–50% is suitable for a good balance of properties in a high shear adhesive.<sup>49</sup>

The shear resistance of adhesives is, of course, temperature dependent and evidence of high cohesive strength often involves measuring holding power at elevated temperatures.

### TEST METHODS

Sources for standardized test methods for evaluating PSA products are The American Society

for Testing and Materials (ASTM) and the Pressure-Sensitive Tape Council (PSTC). In addition a large number of test methods are offered by the U. S. Government,<sup>50</sup> foreign agencies, and organizations representing various segments of industry. Tape manufacturers in descriptions of their products most often refer to results given by ASTM and PSTC test methods.

Both peel adhesion and shear resistance tests utilize tape specimens, while tack testing can be performed on specimens in other shapes as well as on tapes. In peel and shear tests a stainless steel panel with a specified surface roughness is used as a test surface.<sup>51</sup>

### Tack Testing

Although tack testing using a flat probe (probe tack) is almost universally the choice in scientific literature, industry literature frequently refers to a rolling-ball tack test.

Probe tack conditions are set forth by ASTM<sup>52</sup> and the Polyken Probe Tack Tester, shown schematically in Fig. 9, is the most commonly used instrument. In this device, developed by Hammond,<sup>53</sup> a 5 mm diameter flat-ended rod, connected to a load cell, constitutes the probe: The instrument mechanically lifts the

probe to make contact with the PSA, holds it there for a preset time of contact, variable in 10 steps from 0.1 to 100 sec, and then withdraws the probe at a controlled speed, which can be varied in steps from 0.02 to 2 cm/sec. The adhesive, on some backing, is attached to the flat bottom of an inverted metal cup with a hole in the bottom through which the probe enters. Thus, the contact pressure can be varied by using cups or annular weights of various masses. The probe material can be varied, but a stainless steel probe is almost always used. The most commonly reported test conditions are 100 g/cm contact pressure, 1 sec contact time, and 1 cm/sec withdrawal speed (100, 1, 1).

Probe tack value is the force required to remove the probe, as measured by a mechanical-force gauge, under the specified conditions of test. This force will depend, as discussed earlier, on how good a bond is made in the first place and on the rheological behavior of the adhesive when the bond is broken. For example, a highly compliant PSA, which can achieve a good bond quickly, will give a higher tack value at short contact time than will a PSA of higher modulus or viscosity; this distinction might not be observed if longer contact times were used in the test. The ability of the Polyken Probe Tack Tester to vary test conditions permits it to be used for research purposes as well as comparative testing.

Probe tack values increase somewhat with adhesive thickness but reach a constant value at thicknesses above 0.25 mm.<sup>53</sup> The values are also influenced by the nature of the backing, because some of the force measured in bond breaking involves energy expended in deformation of the backing, and by the roughness of the adhesive since more time is required for a rough adhesive to make intimate contact with the probe.

Experimental values of probe tack are expressed in terms of gram force, with all conditions specified. Values of 500 g (for 100, 1, 1 conditions) are considered good. Some very tacky adhesives, particularly rubber-based types, give values as high as 1500 g.

The rolling ball tack test consists of a ball rolling down an inclined ramp and contacting a firmly held horizontal tape strip butted against

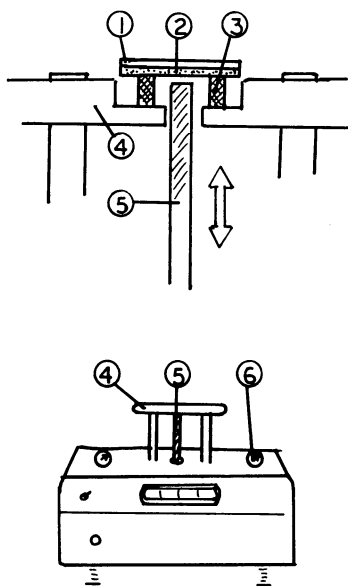


Fig. 9. Schematic of Polyken probe tack tester showing detail of contact area. 1, backing; 2, adhesive; 3, weight; 4, carrier; 5, probe; 6, timing control.



the end of the ramp. The distance the ball rolls on the tape before stopping is the experimental value of tack. The test has a long history and many variations have been explored;<sup>54</sup> many versions are still in use, so that conditions for the test may differ among laboratories. Even between the two standardized versions of ASTM<sup>55</sup> and PSTC,<sup>56</sup> which are supposedly identical, there is a slight difference in the slope of the ramp.<sup>54</sup> Fig. 10 is a schematic drawing of the PSTC apparatus.

Variables explored in the test include the size and weight of the ball, its velocity at the end of the ramp and the shape of the ramp. The current standard methods use  $\frac{7}{8}$  inch diameter steel balls (which are carefully cleaned before reuse to remove any adhesive residues), a ramp which is inclined  $22^\circ$  from the vertical and a release point on the ramp, which determines the velocity, about 6 inches from the bottom.

Using PSTC Test Method No. 6, rolling ball tack valves for commercial adhesives vary from about 0.1 inch to about 10 inches; anything under 1 inch is considered evidence of a tacky PSA.

The term *quick stick* is also frequently equated with tack; it is defined by PSTC as: "Ability of tape to adhere to a surface instantly, using no pressure other than weight of

tape itself. It is measured as the force resisting peeling of tape at  $90^\circ$  from a standard surface upon which it has been applied under no other pressure than the weight of the tape itself."<sup>57</sup> The PSTC test method for quick stick, also known as the Chang Test,<sup>58</sup> utilizes a special jig to permit pulling the tape, laid "without pressure," from a test panel at 12 in./min at a constant  $90^\circ$  angle of peel. Unfortunately, as a tape is pulled from a flat surface there is a zone of compression just before the point where the adhesive parts from the surface.<sup>59</sup> The resultant force has the effect of pressing the tape against the panel so that the condition of using "no pressure" is violated. Further, a stiff backing could prevent the adhesive making good contact with the test surface. Essentially, then, this test resembles a typical peel test and is often not a measure of quick stick, as the term is defined, or tack.

### Peel Adhesion Testing

The force required to remove a tape from a surface depends on the angle of peel, the rate of pulling (see Fig. 7), the roughness and surface energy of the test surface, the pressure with which the tape is applied to that surface, the time of dwell before the test is started, and, as discussed earlier, the mode of failure (see Fig. 6). Moreover, the nature of the backing effects the values obtained.<sup>57</sup> For valid comparisons between tapes, therefore, it is essential that the conditions of peel testing be specified and, if adhesives are to be evaluated, the backings of the tapes be the same. Nevertheless, if conditions of a standardized test are followed, the test can be of great practical and theoretical value.

The PSTC procedure<sup>60</sup> specifies angle of peel ( $180^\circ$ ) and rate of peel (12 in./min), and application pressure is controlled by passing a standardized rubber-covered roller over the one-inch wide tape specimen, placed on the clean steel panel, five times in each long direction. The peel test according to PSTC is to be conducted within one minute of bonding, although many laboratories run the test also after long periods of dwell. Today almost all testing utilizes a constant rate of extension machine, such as an Instron (Canton, MA).

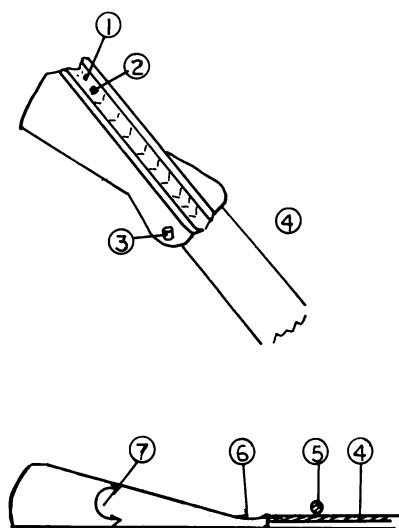


Fig. 10. Schematic of PSTC rolling ball tack tester. 1, V-shaped trough; 2, release mechanism; 3, leveling bubble; 4, tape specimen; 5,  $\frac{7}{8}$ " diameter steel ball; 6, base curve; 7, angle of  $21^\circ 30'$ .

Values are expressed as ounces per inch (most specimens are one inch wide). Acceptable tapes, depending on end use, may have peel values as low as 25 oz./in. while tapes designed for use in high shear applications give values as high as 100–150 oz./in.

### Shear Resistance Testing

The classical test for shear resistance consists of attaching a weight to a strip of tape attached to a vertical panel and noting time for failure of the bond. Since this "holding power" test is highly dependent on the area of adhesive contacting the test panel, the PSTC test<sup>61</sup> specifies a one inch square surface bonded to a steel panel. A rack holds the panels 2° from vertical so that the back of the panel forms an angle of 178° with the extended piece of tape (Fig. 11) in order to avoid any peel-back forces. Failure can be defined as slippage of the tape by a certain distance or complete separation of the tape from the panel. In the latter case a device to automatically time the fall of the weight can be used.

The manner of separation of the tape can be instructive; an adhesive of low cohesive strength or poor resistance to creep will split or leave residue on the panel, while an overly crosslinked adhesive or one too high in bulk

viscosity to permit establishment of a good bond will often fail suddenly (pop off) and leave no residue on the panel.

What constitutes acceptable shear resistance for a tape depends, of course, on the intended use for the product. Thus various weights can be attached in the test and the temperature of test can be varied also. The most commonly reported test weight is 1000 g, for a 25 × 25 mm area of contact. Holding at room temperature (70°F) for over 1000 hours would be considered evidence of adequate cohesive strength. For many tapes, designed to be used at higher temperatures, the holding power test is conducted at some elevated temperature; 100°F or 150°F are frequently used in individual laboratories.

A related test, involving measuring shear resistance as a function of temperature (S.A.F.T.), is often used to compare adhesives; here the vertical tape with attached weight is left in an oven while the temperature is raised (usually 40°F/hr) and the time and temperature at which the tape unbonds are recorded. Higher temperatures at which failure occurs obviously indicate greater shear resistance.

### Miscellaneous Tests

Many additional tests, too numerous to discuss in detail here, are conducted by users and producers to assess tape performance in some particular application. Many, of course, are modification of the more popular tests described above but presumably measure more accurately the resistance of the tape to forces encountered in some special application. For example, there is a test for holding cardboard panels at 90° to each other under stress<sup>62</sup> which is of value for packaging tape. Many others have been developed by the Federal government, by automotive manufacturers, or by associations serving the needs of some industry. Other tests measure such things as adhesion of the tape to its backing, the difficulty in unwinding a roll of tape,<sup>63</sup> and behavior of the tape under various environmental conditions. PSTC alone offers over 30 test methods and hundreds more could be culled from sources mentioned above.

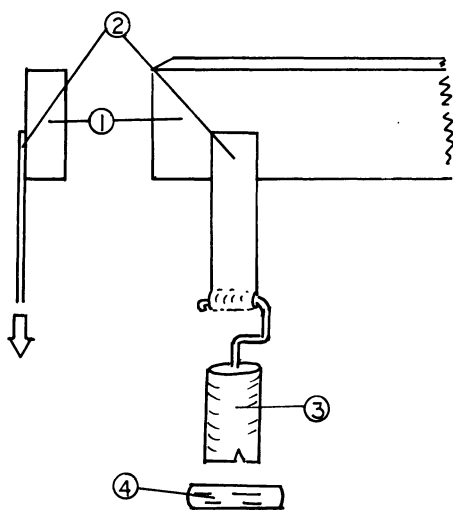


Fig. 11. Schematic of PSTC holding power test. 1, plate; 2, one square inch of tape contacting plate; 3, weight; 4, absorbent pad.

## APPLICATIONS

The versatility of pressure-sensitive products is so enormous that complete tabulation of all their uses is virtually impossible. Every sector of the economy uses PSAs in one form or another. All that can be indicated here are some of the major applications.

### Tapes

As pointed out earlier, tapes constitute the dominant usage form of PSAs. Some of the important tape applications include packaging, masking, splicing, electrical insulation, heating and air conditioning duct sealing, holding or bundling, mounting, and attaching medical and first aid products to skin. Many consumer uses for tapes, familiar to the layman, parallel industrial uses. For example, masking tape is used for painting both in the home and in industrial plants. Frequently, the same tape may be used for more than one application, although manufacturers prefer to offer products for specific industries or end use application, even though this may mean only minor differences in adhesive or backing for various products.

High volume uses of tape are presented below, organized by industry.

**Packaging.** The highest volume application of tapes is in packaging. Much tape is used in the manufacturing and sealing of corrugated boxes and in tear strips for cartons. An important backing for such tape is oriented polypropylene film, which has largely replaced unplasticized vinyl film and paper tapes. Also of importance are reinforced tapes, mainly with polyester film backing, which have reinforcing fibers embedded in the adhesive. A large amount of tape distinguished solely by being inexpensive, such as paper masking tape, is used for less demanding packaging operations. Freezer tapes for the food industry require low  $T_g$  adhesives to permit application at low temperatures.

**Hospital Usage.** Tapes have myriad uses in the hospital; they cover and protect wounds, hold down dressings, intravenous needles, and surgical drapes, and restrict joint movement by

the patient. Because of the presumed need for high water vapor transmission in skin applications to avoid maceration due to accumulated moisture, many tapes utilize porous backings such as fabrics, both woven and nonwoven, and perforated films. Other backings include transparent film and foams. An interesting use employing reinforced backings is wound-closure strips to replace sutures for minor incisions in the skin.

**First Aid and Health Care.** Many of the tapes used in hospitals are available in drug and general stores. The largest volume item is the finger bandage, available with plastized vinyl and cloth backings, which are mostly flesh-colored but can be decorated or transparent.

A very large tape market of many millions of square yards is for diapers. The common disposable diaper is secured with tapes mounted on attached release liners which adhere to the diaper's polyethylene backing.

Feminine sanitary napkins are held in place by PSA tapes. The size of this market is limited by the popularity of tampons, which do not require fastening to the wearer.

In the sporting goods industry, considered here as in the health field, there is appreciable use of strapping tapes designed to prevent injury as well as to support injured joints or muscles. These athletic tapes, with deformable cloth backings to facilitate ease of wrapping and easy tear, must also have adhesive masses that permit facile removal. The sports industry also consumes tapes for wrapping hockey stick blades and baseball bat handles.

**Graphic Arts and Office Products.** Tapes used as graphic art aids are usually sold through art or office supply stores. Many of these products have symbolic patterns or designs printed on the backing; their use eliminates redrawing the design or symbol. Very narrow tapes in various colors are used for bar graphs, construction layouts, etc.

The product of greatest volume in the office area is the well known clear tape, once known as cellophane tape, usually consisting of an acrylic PSA on acetate film.

In the photographic and electronic areas light-blocking tapes, called stripping tapes, utilize a

transparent red film backing to permit viewing of the underlying surface while blocking out wavelengths of light to which the photographic emulsion is sensitive.

**Electrical Industry.** In addition to the familiar electrician's tape, usually a black adhesive with a stretchable film backing, there are many tapes used by equipment manufacturers for insulation in transformers and motors. These products require PSAs of low conductance. The tapes are rated in terms of temperature resistance. For highest temperature exposure, silicone PSAs must be used with specialty backings like glass cloth, polyvinyl fluoride, Teflon, or polyimide film. Tapes are also used to insulate soldered joints, to secure wire ends and, with fabric backings, to cushion and protect assemblies of wires. Harness tape is used to bundle a group of electrical wires.

Specialty products for the electronics industry include aluminum foil-backed tapes for antistatic shielding and copper foil tapes for electrostatic shielding of circuit boards and microwave components.

**Automotive Industry.** Tapes are used for decoration of automobile bodies, to secure body side molding, and for electrical harnesses, but by far the largest use is for masking of surfaces during painting. Because such masking tapes must resist solvents and baking cycle temperatures, as well as peel cleanly later, crosslinked rubber-based adhesives are widely used.

**Corrosion Protection.** Although steel underground transmission lines are often protected by coal tar or fusion bonded epoxy coatings, a large volume of polyethylene tapes as well as some vinyl-backed tapes are used for corrosion protection. Pipes of large diameter, such as oil line pipes, are usually machine-wrapped in the field just prior to placement in the ground. The tapes are unusual in that the backing is from 12 to 15 mils thick and the butyl-based adhesive is approximately of the same thickness. For the pipeline industry the rolls are 18 in. wide and contain up to 800 feet of tape. There is a reduction currently in domestic pipeline construction but appreciable amounts of pipewrap are exported.

**Construction.** Duct tapes for constructing and insulating heating and air conditioning duct work are a high volume item in the building industry. Much duct tape uses a cloth reinforced polyethylene backing, but a widely used version is a high shear aluminum foil tape. Other tapes are used for temporary holding of various assemblies until a permanent adhesive cures. Additionally, tape is used by painters and electricians during construction. Also, PSA on a foamed backing is used for weatherstripping and to plug gaps in place of a sealant.

**Miscellaneous.** Lead foil-backed tapes are used in electroplating, x-ray plate masking, golf club construction and sound dampening. Double-faced tapes are used to splice material from the end of one roll to the start of the next roll in industries where a web of material is fed continuously to some operation. For the paper industry, a paper tape with a water-dispersible adhesive is used to provide for repulpability of the scrap paper. Masking tapes are used for painting of everything from small appliances to railroad cars. For decoration and marking purposes, stenciling tapes are used. Many products, such as tools, use tape to protect edges and surfaces during shipping. Reinforcing tapes are used in manufacture of wallets, handbags, and shoes.

### Labels and Decals

Manufacture of label stock, the precursor assembly of backing or facestock, adhesive, and release paper prior to printing and die cutting, is similar to tape manufacture, but the properties desirable for the facestock include printability as a major consideration. Labels earlier were classified as permanent, removable, or freezer types but in terms of applications are usually categorized as industrial, data processing, or office retail.

Industrial labels produced as roll stock are used for identification, description, and advertising of the product as well as pricing and constitute by far the largest part of the label business. Huge quantities of labels are consumed by the medical-pharmaceutical, toiletries-cosmetics, consumer, automotive, and

durable goods industries. In addition to primary labeling, secondary labels are applied to advertise specials and to apply price tags. Machines are available, for example for the food industry, to weigh an item and print weight, price, and unit price on the label. Although secondary labeling is almost entirely PSA-based, primary labeling of bottles, etc. competes with the much less expensive water-activated glues. However, PSA label use is expected to grow on the basis that PSA label application is less capital intensive and is much more rapid.

Electronic data processing labels, printed by computers, are almost entirely with paper facstock. Information of many kinds, including addresses, is printed on these labels.

In the office category, a relatively smaller market, both blank and preprinted labels are used for inventory control, inspection, filing and many other purposes. In retail stores, the stamping of prices on containers or packages has been largely replaced by paper labels.

Although paper facstock dominates the label business, a sizable fraction of labels and decals utilize more expensive backings of polyester and calendered PVC backings. Typical applications of the more resistant film products are for labeling of shipping cartons and for attaching nameplates and emblems for appliances and office equipment. Decals, hard to distinguish from labels in terms of function, frequently have facstock that is transparent film or brightly colored and reflective metal foils. Some transparent label stock is used to cover and protect other labels or printing.

### Other Products

PSA-based products other than tapes and labels fall in this category. Such products include sheet goods but also consist of individual items that utilize PSAs for attachment to another surface. Although not as large a business as tapes or labels, the dollar volume of these products is many hundreds of millions of dollars. For many products a release liner is an essential component.

A large market exists for PSA-coated sheets used to protect plastic or polished metal surfaces during transportation. An adhesive for

clean peel is essential; paper and polyethylene are common backings.

Reflective signs used outdoors for traffic control and direction signs indoors are mounted or attached with PSAs.

An important article of commerce is wood-grained vinyl sheet, used both for automotive interiors and station wagon bodies. The printed vinyl is used for decorative attachment to many other surfaces.

Hospital usage of nontape PSA products is fairly extensive. Wound dressings of all kinds and sizes are held in place with PSAs. A relatively new product consists primarily of a transparent and elastomeric polyurethane film of high moisture vapor transmission rate coated with adhesive. Among other uses the material can be applied to the skin and surgical incisions made through it under sterile conditions. PSA-held devices are used for ostomy seals and for transdermal drug delivery; in the latter case the drug may be contained in or go through the adhesive. Disposable electrocardiogram electrodes are held in place with PSAs. Used both in the hospital and at home are elastic bandages held in place by the PSA coating on one side. Corn pads and bunion protective cushions, sold in the drug store, consist of form-cut foam or moleskin pieces held to the skin by PSAs.

3M's "Post-it" notes are pads of small paper sheets with a strip of adhesive along the top of the back of each sheet. The small sheets of paper which take ink or pencil inscriptions can be attached repeatedly to letters, reports, book pages, etc., without tearing the paper on removal. The adhesive consists of tacky, cross-linked acrylic microspheres which make "point contact" with the paper. See U. S. Patent 3,857,731 (1974). This relatively new product competes very successfully in spite of higher cost with the older practices of attaching notes to paper by staple or paper clip. In the graphic arts office or shop a small amount of film similar in construction to the tapes described before but of larger size is consumed; the film sheets can be cut into pieces of any desired size or shape.

A fairly large market exists for decorative shelf and drawer coverings. Used to a large extent by the homeowner, these vinyl sheets which can be cut to size from a roll offer pro-

**Table 10. Adhesive Thicknesses for Various PSA Products.**

Product	Approximate Coatings Thickness (mils)
Paper labels	1.0
Paper transfer tape	1.0
Plastic labels and decals	1.0-1.5
PVC finger bandage	1.5-2.0
Silicone electrical tape	1.5-2.0
Diaper tape	1.5-2.0
Polyester packaging tapes	2.0-3.5
Polypropylene strapping base	2.5-4.0
Acetate office tape	2.5-3.0
Aluminum foil duct tape	2.5-3.5
Printable computer tape	3.0
Porous hospital tape	3.0-4.0
Trainers tape	4.0-5.0
Velcro strip	5.0-7.0
Glass-reinforced polyester tape	5.0-7.5
Film labels and decals	6.0
Paper masking tape	6.0-7.0
Coated cloth packaging tape	12.0
Corrosion protection tape	12.0-15.0

tection of surfaces while serving an aesthetic purpose when placed on furniture, shelves, etc. Also used in the home are floor tiles coated with a PSA. Most floor tile manufacturers make vinyl tiles which are backed with a thick PSA coating, usually of an inexpensive composition based on something like atactic polypropylene or EVA because the tile experiences little of shear forces after placement. Also available for flooring installations are carpet and wood squares coated on the back with a PSA.

Lightly metallized polyester films are placed over windows to help reduce the sunlight passing through the window. Most of these solar radiation control films are coated with a PSA for attachment.

The ubiquitous "Velcro" is often attached to surfaces via PSAs. For example, car interior head liners are secured to Velcro pieces attached to the car roof by a shear resistant PSA.

### Adhesive Mass Thicknesses

The weight or thickness of adhesive masses applied to various backings depends both on the method of application and the intended use of the product. Thus coatings applied by oven-drying are generally thin, roughly 1-3 mils,

whereas calendered coatings are generally over 4 mils in thickness. Further, cloth or other porous or nonsmooth backings often require a heavier coating weight to compensate for the adhesive that penetrates into the backing. Table 10 gives typical adhesive thicknesses for various products.

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# Bonded Abrasives

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Modern civilization would not be possible without bonded abrasive products. By the year 1825 sand, emery, and even diamond were being bonded together with shellac for use in abrasive sticks and wheels. Rubber bonded wheels were introduced in 1857, the sodium silicate and the vitrified bond just after the Civil War,<sup>1</sup> and the phenolic resin bond in 1923. The metal bond was introduced for diamond wheels in 1940.

Bonded abrasive products have a three-dimensional structure consisting of abrasive particles, a bonding agent, and porosity. Each of these three elements may be varied in amount in a precisely controlled fashion to alter the behavioral characteristics of the abrasive article in predictable ways. Bonded abrasive articles may take the form of sticks, wheels, wheel segments, and variously shaped cylinders, cones, balls, etc., to which are affixed metal rods for insertion into chucking devices of power tools. A bonded abrasive article, being three-dimensional in concept, operates sacrificially during use, with retention of sharpness until all the usable portion has been worn away. In contrast, a coated abrasive product must be discarded when its single abrasive layer loses its sharpness.

## THE ROLE OF THE BOND

The grinding quality of a bonded product in any given application is determined by the choice

and amount of abrasive and the choice and amount of bond. Since this is a discussion of adhesives, other sources should be consulted for information about abrasives.<sup>2</sup>

In a bonded abrasive product the prime role of the bond is that of a structural adhesive. The function is to hold the abrasive particles in some desired spatial relationship and to provide mechanical strength and integrity to the composite. Other functions may be designed into the bond, however; it is upon these other functions that the complexity of bonded abrasive technology depends. The bond may be required to provide a strong, tough, thermally resistant wheel for very difficult grinding jobs when rugged durability is needed. Again, it may need to be friable or thermally sensitive or weak for free and fast cutting action, good finish, or low metallurgical damage to the work. It may need to resist water or alkaline coolants.

In the grinding of many metals, reaction of the freshly cut metal surface with air forms an oxide layer which can effectively prevent adhesion of the metal surface to the abrasive, to the bond, or to itself. This facilitates the abrasive process. Substances which can react more rapidly with fresh metal surfaces than does air, or which can melt and cover the surface with a protective layer, are called *active* grinding aids. The most common ways such substances are used is in the oils or water-based coolants for wet grinding and as impregnants or fillers in the bond of the abrasive article for dry grinding.



Through careful selection of fillers and filler combinations, the grinding quality of the bonded product may be greatly improved. Fillers known to be effective are cryolite, fluor-spar, fluoborates, sulfur, iron disulfide, polyvinylidene chloride, polyvinylchloride, tin, and compounds of lead and antimony. Active fillers cannot be incorporated into metal or vitrified bonds directly because of the nature of these bonds and their high temperature processing. However, wheels which contain accessible and interconnecting porosity may be impregnated after manufacture with various materials to strengthen them, to provide lubrication, or to provide active grinding aids. Thus epoxy resins, fats, waxes, graphite, and sulfur are frequently incorporated into vitrified wheels and occasionally into organic bonded wheels. Organic bonds such as phenolic lend themselves conveniently to the incorporation of particulate active fillers such as iron pyrite, polyvinylidene chloride, cryolite, and potassium compounds such as potassium sulfate or potassium fluoborate.

## APPLICATION

The widespread commercial use of both coated and bonded abrasives has been very dependent on machine development, although these tools evolved on the basis of hand methods which are still in use. A grinding wheel (or a coated abrasive belt) must be mounted on a machine, however simple or complex, in order to have it perform its basic function.

Existing wheel grinding machinery ranges from low or even fractional horsepower and hand operation on light equipment such as a dental drill or a  $\frac{1}{2}$ –3 horsepower portable grinder up to roll, centerless, or slab grinders powered by as large as 200–300 and even up to 500–600 horsepower motors. Paper pulp grinders may be powered by motors as large as 10,000 horsepower.

Grinding operations may be sorted into four main categories: fixed feed, fixed force, constant power, and cutting off. The choice of bond type and wheel specification for a given operation is determined by the specifics of the operation, the available power, speed, wet or dry environment, and work material; and by re-

quirements for the finished part of dimensional accuracy, finish, and surface condition of the part. This information leads to the selection of the grinding wheel composition which includes kind, size, and shape of abrasive; volumetric proportions of abrasive, bond, and porosity; bond composition; fabrication process; and aftertreatments and/or mechanical inclusions.

Rubber, shellac, and alkyd resin bonds are inefficient. However, they are used for fixed feed, fixed force, and cutoff operations on applications where there are requirements for very good finish, no metallurgical damage to the part, where only limited power is available, or perhaps very fast cutting is required.

Phenol-formaldehyde (resinoid) bonded wheels represent by far the largest part of organic bonded products. These are standard for dry, rough, fixed force, or constant power grinding in foundries and steel mills. Here high speeds are the rule and toughness and durability are required. Speeds of 16,000 surface feet per minute are common. Resinoid wheels are widely used in cutting-off operations, where strength with flexibility (break resistance) is required. The trend toward higher speeds has been more rapid in cutoff than in any other type of grinding. There is also a trend to substantially higher rotational speed and grinding speeds in drill grinding and camshaft grinding.

Vitrified bonded wheels make up roughly half of all those produced, although the recent trend toward higher speeds is causing some shifting toward resinoid bonds. Vitrified bonds are standard for most fixed feed operations because of their dimensional stability and predictability, their utility in wet environments, their free cutting nature, and their friability, which allows them to be readily shaped or “dressed” to maintain grinding geometry or sharpness. The brittleness of these bonds and their heat shock sensitivity precludes their use in many applications such as cutoff.

The use of metal bonds is reserved for the most difficult grinding operations, where maximum strength, durability, and thermal resistance is required and exotic abrasives such as diamond are justified as the abrasive. Most of this is fixed feed operation. Metal bonded cutoff wheels, represented by metal bonded diamond segments brazed to the periphery of a

steel disk, are used for very difficult cutting operations, especially on nonmetallics such as ceramics, carbides, and cermets, stone, and reinforced composites.

## ORGANIC BONDED PRODUCTS

The organic bond grouping includes a number of subsystems based on very different polymers and curing mechanisms. There is little use in the bonded abrasive industry for bonds of a thermoplastic nature, partly because of an undesirable tendency for thermoplastics to smear and also because of the superior ability of thermosetting systems to resist time dependent changes such as creep and environmental stress crazing.

Commercially available organic bonds include ones based on phenolic and modified phenolic resins, alkyds and polyesters, shellac, polyurethanes, epoxies, and rubbers such as natural, synthetic natural, GRS, Neoprene, and acrylics. Further, polyimide bonds find use in diamond and cubic boron nitride products.

These bonds provide a very wide range of composition and of thermomechanical properties. The relatively low curing temperatures range up to 225°C, except for those few bonds containing refractory polymers like the polyimides, which may reach approximately 400°C. These relatively low curing temperatures permit inclusion of thermally sensitive materials which could not survive the processing conditions for metal bonds (650°C) or vitrified bonds (up to 1250°C). Moreover, the hot versus cold strength of cured organic bonds can be manipulated through choice of composition and curing conditions in such a way that grinding properties can be varied differently from mechanical strength. Additionally, the higher strength obtainable with organic bonds allows the use of organic bonds at very high and efficient centrifugal speeds not economically or technically feasible for either vitrified or metal bonds.

### Organic Fabrication Methods

Organic bonds contain varying amounts of finely divided (usually mineral) filler dispersed in a thermoset polymer matrix. The matrix is derived from combinations which may include

liquid resins or monomers, rubbery or plastic intermediates, and particulate solid resins. Additives such as catalysts, accelerators, plasticizers, coreactants, and processing aids are frequently included, and various mixing techniques are used both for bond and mix preparation. Usually the main bond components are blended first, after which the abrasives and bond are combined into a mix for molding.

In a typical procedure for making a mix, the abrasive is wetted in a mixer with a liquid wetting agent which may be either a coreactant, a plasticizer, or a solvent for the resin. Then a powdered resin bond is added and the mixture stirred so that the powder may be coated onto the wetted abrasive particles to form a dry mixture. The degree of pickup of the powder onto the wetted abrasive granules is determined by the proportions of liquid and powder used. Such a mix is relatively free-flowing and can be distributed readily and uniformly in a cold compression mold.

Plastic or rubbery ingredients for bonds require more vigorous mixing than simple stirring can provide. Kneaders, banbury mixers, or roll mills are used to blend bond ingredients and to prepare the abrasive mix for such bonds. Mixes which cannot be spread or packed into a mold readily may be rolled out into sheets, much like the sheeting of rubber compounds, from which product shapes may be cut. Some few bonding systems are liquid, and these may be poured into molds with or without vacuum treatment to remove bubbles.

Compression molding to thickness, to predetermined pressure, or to closed mold is the main molding method for most products. Mixes for cold molding must be formulated to provide greenware strength for product between molding and curing and to allow the porous green wheel to be cured without becoming distorted through evolution of volatiles which may cause swelling or through slumping because of a bond which is too low in viscosity at temperatures before geometry is fixed by the cure.

Stronger and more dense products can be obtained by hot compression molding, usually in a flash mold. For phenolics, a press platen temperature of about 165°C is usually used. Such a hot molding cycle can be used either to fix the wheel geometry into a partially cured con-

dition for subsequent oven cure, or it can be used to provide the sole curing cycle for the product.

In recent years there has been an industry trend to simplify the production of abrasive products and to reduce production costs through development of liquid casting systems. Commercial processes and products have been developed based on polyurethane bonds and more recently on epoxy bonds. Much remains to develop the potential of such liquid abrasive bonds for the abrasives industry.

### Bond Characteristics

**Shellac.** Shellac bonds are not the form of shellac most people know as a solvent-based coating. Shellac bonds for abrasive products have been subjected to extensive baking for long time (days) in order to convert the shellac by ester condensation reactions into a strong, tough, relatively water resistant bond which has special thermally sensitive properties. This toughness, good adhesive properties, and high thermal sensitivity provides a very fast and free-cutting action. This gives a high quality of cut, absence of heat damage to parts ground, and high luster finish unmatched by any other bond system. Its fast wearing characteristics and limited strength range are causing it to be replaced by rubber and other organic bonds.

**Rubber.** Rubber products combine many of the cutting characteristics of shellac with the greater strength, water resistance, and heat resistance available in the rubber bond. Most rubber bond systems are of the high sulfur hard rubber type. However, physical properties of the rubber bond can range from soft and elastically conformable to high modulus with high tensile strength. These differences can be achieved through appropriate choice of rubber types, sulfur content, coreactants, and fillers. The rubber system lends itself readily to the incorporation of active grinding aids either as fillers or as integral components of the polymer structure (such as organic halogen and sulfur compounds).

**Phenolic.** Although substituted phenols and agents other than formaldehyde occasionally

find use in resins for phenolic bonds, the backbone of the phenolic abrasive bond system is the phenol-formaldehyde reaction product, either as a resole or as a powdered novolak crosslinked with hexamethylene tetramine. For maximum strength and rigidity over a broad temperature range, this polymer system has little competition. No other system has been able to match its structural and thermomechanical properties on a cost/performance basis.

The high compatibility of both the phenolic resin intermediate and of the crosslinked material with a wide range of organic and polymeric substances has permitted further wide variation to be built into bonded abrasive products. Materials such as epoxies, various rubbers, polyvinyl chloride, polyvinyl formal, or polyvinyl butyral may be combined with the phenolic material either in the resin kettle or later in preparing the abrasive bond or mix. Such modifiers can provide greater toughness and water resistance and can impart a softer grinding action and higher bond quality while rotational strength and break resistance are retained.

**Epoxy Bonds.** During the past twenty years or so numerous companies have developed commercial bonded abrasive products based on the epoxy resin system. Cold or hot pressed products based on powder mixes have been developed from powdered epoxies used in powder coating technology. Examples are powderable resins based on bisphenol-A and on brominated bisphenol-A. Other examples are products prepared by casting of liquid epoxy mixtures of abrasive, fillers, and sometimes bond-softening agents such as plasticizers and hollow materials such as polystyrene beads or phenolic or glass microballoons. Liquid casting of abrasive wheels seems particularly attractive for wheels of large or complex shape difficult to form by compression molding. Such liquid systems also seem of special attraction for very small or complex shaped wheels containing very fine abrasives. Such products could be made in reactive injection-molding-type operations.

The variety of both liquid and powderable materials available and their wide range of cured properties along with relatively low costs

make epoxy resins attractive for adaptation for use as abrasive bonds. The epoxy bond should be viewed as generally lying above shellac, alkyd, and rubber in bond strength and heat resistance but below that offered by the phenolic bond system.

**Specialty Bonds.** The polyurethane system can be formulated over a wide range of cross-linking densities and mechanical and thermal properties. Little use has been found for this system in bonded abrasives. A bond based on this system was developed perhaps twenty years ago and found some commercial success in the rough grinding of large milling rolls, where deep cuts, high wheel speeds, and high stock removal rates are found. Some usage was also developed in other high speed grinding operations. However the business was not a commercial success, and such products are no longer available.

Other bond systems have been based on alkyds, unsaturated polyester resins, and polyvinyl alcohol. Although such bonds can be formulated to be strong, they have usually found application where a very mild or free-cutting action is required or where an extremely fine abrasive is required. Examples are knife grinding, hypodermic needle pointing, the finishing of rotogravure and milling rolls, and the cutting off of very difficult-to-grind materials.

The great variety of high performance polymers now available, especially those designed for use at temperatures beyond the range of ordinary organic materials, has encouraged much effort in evaluation of these for bonded abrasive utility. Of these, only the polyimide family has found its way into abrasive usage. The polyimides, polymaleimides, and polyamideimides have many useful properties such as high strength retention at high temperatures, toughness, resistance to a wide variety of solvents, and abrasive resistance or lubricity. Because of high cost and difficult fabrication requirements, these materials have found only very specialized application where their unique properties can be used to advantage. Two such applications are polyimide bonded diamond wheels used in cam and in drill flute grinding.

## VITRIFIED PRODUCTS

Vitrified bonds are very widely used in the metalworking industry, especially for machinery manufacture. The basis for this glass type bond is a fusible clay, feldspar.<sup>3</sup> Refractory materials and fluxing agents are added to produce the desired composition. The dried clay and other bond ingredients are pulverized, screened, and blended to form the dry bond. This is added to the water wetted abrasive in a mixer to coat each abrasive particle with the bonding medium. The resulting mix is pressed cold in compression molds to form the basic wheel shape.

To provide mechanical strength sufficient for handling of the unfired wheels, various organic polymeric materials may be used to wet the abrasive, such as starch paste, dextrin, and urea- or phenol-formaldehyde resin. During firing, these organic substances decompose to yield carbonaceous char residues which provide temporary binding strength for the wheel until the glass bond sinters or melts and develops its own vitreous strength. These residues must then burn off to leave no unwanted discoloration or deterioration of the bond.

After air drying, the cold pressed green wheel is fired in a kiln, either batch or continuous, to about 1250°C for the appropriate time.

The original vitrified bonds tended to have a limited range of firing conditions under which satisfactory product could be made. The current trend is to make bonds from glasses which have a broader firing range and which result in greater uniformity in the product.

Silicate bonded wheels, wherein the bond consists essentially of sodium silicate with fillers, are mixed, spread into molds, and tamped to compact. These are fired at considerably lower temperatures (about 260°C) and are not as strong as vitreous bonds. They are used when very free-cutting action is required and when the machine conditions (such as low rotational speed) permit. Very large wheel diameters can be made with such a bond system. The silicate bond has been replaced largely by stronger and more versatile products.

The oxychloride bond, a mixture of magnesium chloride and magnesium oxide, has had

some minor success. This bond sets cold and requires no bake. Like the silicate bond, this system provides a soft, free-cutting action. However, it is not resistant to attack by coolants, and this has seriously restricted the utility of this bond system.<sup>4</sup>

## METAL BONDED PRODUCTS

Metal bonded wheels are made nearly exclusively with diamond for very severe applications where high mechanical strength is required. Electroplated cubic boron nitride products are also finding applications, especially of very difficult to grind and very hard steels.

Metal bonded products are produced by mixing the abrasive with powdered metal and cold pressing the mix into the desired shape, after which it is sintered in an inert atmosphere. Alternatively, the abrasive are mixed with metal powder and hot pressed. Products are even prepared by cold pressing the diamond and metal powder mixture and subsequently infiltrating with molten metal. Another method is electroplating, wherein the abrasive is affixed to a metal mandrel by means of a metallic layer electroplated around the particles of abrasive to lock them in place. The bonds employed vary from soft bronze through steel bonds to very durable cemented carbide bonds. Organic-type adhesives have virtually no use in metal bonded abrasive products except for some applications for attaching diamond-containing sintered metal rims to either metallic or nonmetallic cores.

## MISCELLANEOUS ADHESIVE USES

The bonded abrasive article, after it is formed and fired, may still be incomplete or unusable in that state. The use of adhesive materials to bond such articles together or to other materials is common, and a wide variety of adhesive systems have been used.

Such adhesives are frequently room temperature curing, not only for simplicity of use but also because the adherends may be of very dissimilar materials such as vitrified bonded abrasive and steel. The product may be used in a wet environment or be exposed to high tem-

perature during use, so a water resistant and/or heat resistant cement may be chosen.

Probably the largest adhesive operation for bonded products is the cementing of abrasive wheels or segments, especially vitrified bonded products, to a steel plate for mounting on specially adapted grinders. Such an adhesive joint may need to withstand complex thermomechanical and environmental stresses during use. One common method for this adhesive application has been to use a rubbery bond based on a rubber compound. Such bonds have been replaced largely by the use of resilient cements based on epoxy resins. The epoxy resin system can be formulated to provide very elastic bonds either with use of an external plasticizer or, preferably, through internal plasticization with epoxy or hardener components. For plate mounting of wheels when a very rigid and/or heat resistant bond is required, specially formulated filled phenolic adhesives can be used. Both epoxy and phenolic adhesives, when properly formulated and cured, can provide adhesive bonds superior to the bond in the bonded abrasive product itself.

The second largest use of adhesive on finished product is probably that for mounted wheels and abrasive points. Small abrasive shapes are frequently fitted with metal mandrels for mounting in chucks like a drill bit. Although organic bonded materials may have metal mandrels molded in, the high firing temperatures for vitrified products preclude this technique, and the metal mandrels must be inserted and cemented in place afterward. These products may be exposed to severe mechanical abuse and high temperatures during use. Copper oxide-phosphoric acid cement has been used widely here. Other cements have included low melting alloys, phenolic resins, and epoxies.

Pulpstones are used in the paper industry to grind wood into pulp and are of a large diameter (to 6 ft). Once installed, they must provide years of trouble-free service in a hot aqueous environment and so must be sturdily constructed. Vitrified segments, each containing a metal bolt cemented in place with a phenolic resin, or perhaps an epoxy resin, are arranged into an annular ring affixed to a metal rein-

forcement cage and separated from one another with a layer of resilient material, such as a rubber compound. Phenolic resin and epoxy compounds have also been used for this purpose. After the abrasive ring has been fabricated, the wheel is completed by casting a concrete core inside.

Room temperature curing systems such as unsaturated polyesters and epoxies are frequently used to cement threaded bushings into wheels. Inorganic materials such as litharge and sulfur cements and low melting metals are used for anchoring and bonding operations.

Injection molding compounds are occasionally used to form bushings and mounting pads on abrasive wheels.

Rubber and cellulosic-type solvent cements are used for attaching gaskets and blotters. Water based adhesives such as sodium silicate, starch, dextrin, and latex are used for a variety of applications such as labeling.

Grinding wheels with accessible porosity may be impregnated with liquid curable resins to strengthen the product or to reduce abrasive action on machine mounts. Such an impregnation of a vitrified wheel for example with an epoxy resin can greatly increase not only the compressive strength but also the rotational burst strength of the wheel and allow higher operating speeds to be specified.

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# Coated Abrasives

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A coated abrasive consists of a backing substrate coated with an abrasive mineral (grit), which is bonded to the backing using an adhesive system. There can be several layers of adhesives used in the manufacturing process. The primary adhesive coat, called the *make* coat, is used to bond the grain onto the backing. A top coat of adhesive is applied after the make coat and grain coating. This is called the *size*, since it is used to reinforce the grain and insure an adequate abrasive bond. Reactive fillers are also incorporated into the size formulation to enhance the grinding performance of coated products.

The backing substrate, especially if it is finished cloth, may also contain several layers of adhesives and fillers, which are used to impart to the backing its desired body and other required properties.

Coated abrasives are made in a wide range of grit sizes, ranging from as coarse as 16 grit to very fine micron and submicron sizes. They are also made available in a wide array of different shapes and sizes. The most common includes sheets, disks, rolls, flap wheels, and belts.

Coated abrasives are different from bonded abrasive wheels in that coated products have abrasive grain coated on their surface, as opposed to bonded products, which are comprised of mainly abrasive grain bonded together to form the actual shape of the product. Coated abrasives are designed to be used only on their

surface, while bonded abrasives are designed for total cut and breakdown, thus exposing new abrasive particles to continue the grinding process.

## HISTORY

The first coated abrasive made goes back to the 13th Century, when the Chinese used crushed seashells as an abrasive grain and bonded them to parchment paper with natural gums.<sup>1</sup> Other forms of coated abrasives were made by applying abrasive minerals to animal skins, leather, etc., and as time passed, animal hide glues and varnishes were used to bond grain to paper and cloth.

Today's coated abrasives have advanced from a simple smoothing and polishing function to complex heavy stock removals where rates of 5–7 in.<sup>3</sup>/min per linear inch of belt width are not uncommon, thus rivaling traditional grinding wheel applications. Since modern backing designs have been improved to keep pace with advancements made in abrasive materials, coated abrasives are now able to compete effectively in some of today's most demanding abrasive applications.

Modern day abrasive grits have also progressed from natural minerals to synthetic abrasives, which include alumina-zirconia and ceramic aluminum oxide abrasives. Conventional aluminum oxides are still widely used; however, these new abrasive materials are

much tougher and greatly improve the ability to effectively abrade large amounts of material. Silicon carbide still is widely used in the traditional applications where razor-sharp hardness is required.

In order to take advantage of the new abrasive grit materials, new and improved bond systems had to be developed. Subsequently, adhesive systems have also come a long way, progressing from fish and animal hide glues to urea-formaldehyde resins, epoxies, phenolic, and radiation-curable systems. This evolution has placed a continuing demand on the adhesive systems used in the manufacturing of abrasive products.

## BACKINGS

### Types of Backing

Coated abrasive products can be made on a wide variety of backing types. There are five general groups of backings used in the coated abrasive industry: paper, cotton cloth types, vulcanized fiber, synthetic fabrics and films, and any combination of these laminated together. Generally speaking, *paper*-type backings are used when strength and toughness are not required, but low cost is essential. *Cotton cloth* backings are used where greater strength and heat resistance are required and cost is again a significant consideration. *Vulcanized fiber* backings are used for disk application where the backing must be stiff and have good strength in all directions. Typical fiber that is coated is 0.030 in. (30 mils) in thickness and is used primarily for portable grinding applications. *Synthetic fabrics* are usually polyester, polyester-cotton, rayon, or polyester-nylon blends, while films are usually polyester. The synthetic materials have the greatest physical strength and toughness, and are used in the most demanding applications where performance is the most important consideration. The use of these backing materials requires that the end user have good control over his or her operations, so that these premium products are utilized to their fullest. The last group involves *combination* of the above in order to meet special requirements that none of the other backings would meet alone. Usually these combinations are used where the abrasive prod-

uct needs to meet increasingly tougher applications or special finishing requirements.

Specifically, of the various backing types, greige goods (raw cloth substrate from the cloth mill) can produce many different types of finished cloths. Furthermore the same greige goods may be finished differently to create a backing with completely unique properties. Backings may also be classified by their weight and the type of weave used to make them. For example, a backing could have a plain, twill (drills and jeans), sateen or knit construction.

### Cloth Filling Adhesives Systems

Adhesives used in cloth filling range from plain animal hide glues and starch based systems to complex thermoset and radiation-curable systems. Extensive use is also made of latex systems of various polymer and copolymer blends, which impart to the backing good adhesion and flexibility not obtainable with glue- or starch-based systems. Typical latex systems used for cloth filling are based on synthetic rubbers, vinyls, or acrylics. These systems are often modified with fillers such as calcium carbonate and thickening agents to give the backing its desirable properties.

Radiation-curable resins are also finding use as cloth filling systems. Both ultraviolet- and electron-beam-curable systems are used today and offer some unique properties. One advantage of these systems is that they are energy efficient, that is, they require minimal amounts of energy to be polymerized. Another important advantage is that radiation-curable resins are in effect 100% solids. By using reactive monomers (instead of solvents) as diluents to cut viscosities of the base oligomers, airborne emissions can be virtually eliminated. A third advantage is that these systems cure immediately after exposure to the radiation, requiring no heat. However, reactions are exothermic during polymerization.

The most commonly used radiation-curable resin systems for cloth finishing are based on acrylated epoxies, acrylated urethanes, and patented hybrid systems which form interpenetrating networks.<sup>2</sup> Mixtures containing 25–40% phenolic or other heat-curable resins are particularly useful.





imal glues used are obtained in a dry granulated form, and are prepared in water. Hide-based animal glues are the most widely used in the abrasive industry, and may be modified with fillers, plasticizers, dispersing agents, etc. Other glues such as bone and fish generally do not have the jelling properties that hide glues possess.

Glues are easy to apply, and reach a jelled consistency on cooling slightly from their heated state during application. This fast jelling aids in anchoring the grain in place, and provides abrasive products with good grain orientation. Animal glues are economical to use, which is of prime importance on most paper products.

*Varnishes* are used extensively in the manufacturing of waterproof paper products. These products require waterproof bonds with some degree of flexibility. The spar varnishes used today are primarily phenolic-modified tung oils. They are typically made by blending approximately equal parts of tung oil with a resole phenolic resin, along with dryers, usually cobalt and manganese naphthenates. Varnish cures by oxidizing with atmospheric oxygen, which causes the coating to polymerize.

*Urea-formaldehyde* systems are used in products that require more demanding properties. These systems are used on both paper and cloth products. Urea bonds impart better heat resistance and more strength than either glue or varnish adhesives. The urea resins are usually obtained in a liquid form, and are catalyzed by additions of ammonium chloride or other acid catalyst. The fillers must not interfere with the acid catalyst. Typically, calcium carbonate is avoided, but other fillers such as calcium sulfate are acceptable.

*Phenolic* resins are used in paper-, cloth-, and synthetic-backed products. These bond systems give the greatest strength and heat resistance compared to conventional adhesives. Today's high performance coated abrasive products would not be possible without the use of phenolic resins. The typical systems are base catalyzed and water miscible, having water tolerances in the range of 50–300%. Most phenolic make and size bonds are blends of two or more resins, usually a high (e.g., 1.8) and a low (e.g., 1.1) F/P ratio (formaldehyde-to-

phenol) resin. Phenolic systems require thermal curing, which takes place by polycondensation reaction at temperatures in the neighborhood of ~200–250°F. These resins can be B-staged in the maker and sizer ovens prior to final curing, or taken to complete cure in specially designed sizer ovens.

*Radiation-curable* resins also go into make and size formulations. One big advantage of these resins is that they cure almost immediately through a free radical mechanism after being exposed to high energy radiation. In the case of ultraviolet curing systems, photoinitiators are used to enhance the generation of free radicals, which in turn allow the reaction to propagate, thus polymerizing the resins. Electron beam curing methods do not require initiators, because the high energy electrons generate free radicals on being absorbed by the resin itself. Curing of radiation curable systems is usually carried out under nitrogen. If these resins are irradiated in air, curing is inhibited on their surface because atmospheric oxygen terminates the free radical mechanism by the formation of peroxidic structures which are more stable than the radicals generated by irradiation, thus ending the propagation.

Typically, coated abrasives are manufactured on making machines which employ festoon curing ovens, which require large amounts of floor space. Disadvantages of festoon curing areas include the formation of stick marks or defects caused by suspension rods, and binder and abrasive migration. Radiation-curing systems eliminate the need for festoon curing ovens and the defects associated with their use. Because of their rapid curing, there is no need to hang coated material on rack sticks in long ovens to facilitate curing.

Another advantage of radiation curable systems is that they improve the sharpness of the abrasive product by curing immediately, thus anchoring the grain particles in place in the best possible orientation. Thermal cure systems first tend to reduce in viscosity as they are exposed to heat; thus, some loss in grain orientation is possible through resin and grain migration.

Radiation-curable systems are likely to be based on acrylated epoxy resins, acrylated polyurethane resins, acrylated epoxy-novolac resins, and acrylated isocyanurate resins.

## Formulation of Coating Systems

The binders used in the manufacturing of coated abrasive products can be complex. The adhesive systems used in premium coated products must be able to withstand considerable heat, anchor the abrasive grit onto the backing, deliver grinding aids if present, and have a usable plot life of several hours. This means that fillers must be well dispersed, additives must be balanced to give good wetting, with no foaming, and have the proper rheology to be coated without sagging during curing. Typical fillers may include: calcium carbonate, cryolite, potassium fluoroborate, potassium cryolite, calcium sulfate, and zinc stearate. Other filler systems may be used to promote rheological changes, flattening, nonslip, or antiloading properties.

## Use of Statistically Designed Experimentation

Many variables are involved in designing a coated abrasive product, and some way is needed to identify and study their effects. Statistically designed experimentation is the best way to fine tune coating formulations, enabling the optimization of product performance.

For example, it is found that blending two different surface-active agents improves their effectiveness. Through the use of designed experimentation, one can easily determine the optimum levels of each agent, in conjunction with defoamers, dispersants, etc. Combinations of reactive fillers may yield a eutectic mixture with a lower melting point, requiring less energy to activate. During grinding of metals and their alloys, many chemical reactions are taking place simultaneously which affect the performance of coated abrasives. Binder-metal reactions occur when reactive fillers are used to enhance performance. A statistically designed experiment can determine an antagonistic and/or synergistic effects of formulation components on product performance. Mathematical models and computer graphics enable the design engineer to predict the interaction of the components and their effect on product performance.

## APPLICATIONS

### Materials Being Abraded

Coated abrasives can be effectively used on a wide variety of materials, including wood and wood products, plastics, paints, glasses, leather, rubber, metals and their alloys, and composites. The range of materials that can be processed with coated abrasives is virtually unlimited.

### Power Demands

Power demands may vary from hand operations utilizing minimal effort to abrasive planers that consume several hundred horsepower. Because of the wide variety of applications and the vast array of finishing and stock removal requirements, there are many types of coated abrasive designs and products on the market.

### Characterization

Most coated products are used at grinding speeds ranging from 1500 to 11,000 sfpm (surface feet per minute). In-feed pressures vary from less than 1 psi to as high as 800 psi.

Coated abrasives are individually formulated to work under the specific constraints of certain applications, such as wet or dry grinding, carbon steels, exotic aerospace alloys, wood finishing, wood planing, antistatic, antiloading, and polishing applications.

### Contact Wheels

An often overlooked element of application is contact wheels which are used to drive and support the abrasive belt products while controlling the degree of aggressiveness and finish required. Wheels can be made from a variety of materials, such as steel, aluminum, rubber, urethane, and cloth. The most common types are rubber coated aluminum wheels, serrated on their surface. A soft rubber contact wheel will allow the coated abrasive products to cut smoothly, but be less effective in removing stock than a harder rubber wheel. The serrations are designed to improve the coated abrasives' aggressiveness. This usually extends the life of the coated products by reducing the level

of glazing, and by allowing the abrasive product to break down more easily, thus enabling the operator to use the product with less effort. Serrations are used to increase the effective unit pressure on the abrasive surface.

The ratio of land width to the width of a groove machined in the surface of the contact wheel, known as the *land-to-groove ratio*, determines how aggressive a given wheel will be. A contact wheel with higher ratio of land to groove will be less aggressive and give a better finish.

The angle of serration can also be varied to increase or decrease the aggressiveness of the wheel; however, most wheels are used with a 45° angle of serration. Contact wheels can greatly affect the way a given coated abrasive product functions, thus giving even more versatility to coated products.

There are also many applications where contact wheels are not utilized, but depend on some other means of support, for example, platen or slack-of-web grinding methods, as well as hand, disk, and roll operations.

### Versatility of Coated Products

Outside of basic design, any given coated product can be modified by changing its flexing or its application environment, including backup pad or contact wheel, the land-to-groove ratio, the operating speed, and the type or concentration of lubricant if the operation is wet. One significant advantage this provides coated abrasives over bonded abrasives is versatility: a given coated product can be adapted to a wider range of applications than a given bonded product.

Once a product is coated, it can be converted into any size or shape desired, up to the width of the jumbo roll of coated abrasive. It is even possible to exceed the width of the jumbo by making segmented or sectional wide belts. These sectional belts contain more than one splice, and are fabricated from panels cut in the cross rather than the running direction of the belt. Belts can be manufactured in width ranging from  $\frac{1}{4}$ " to 68" in single splice belts, and to 130" width in sectional belts.

### Splicing of Coated Abrasives

Splices are used to join the ends of coated abrasives so that endless belts, or sleeves, can be formed. The two most commonly used types of splices are laps and butts. *Lap* splices are formed by overlapping the ends the abrasive material, after preparing each end and applying the proper adhesive. This is followed by a hot-pressing operation that sets the adhesive. *Butt* splices are less complicated and are manufactured by applying an adhesive to each end of the prepared backing, butting the ends together, and taping them with a special reinforced splicing tape. This also is followed by hot-pressing. Within these basic splice types, there can be many variations depending on the final application.

The adhesives used to make splices are usually polyurethanes. Favored crosslinkers are the trifunctional isocyanates, to give the splice adhesive its final heat resistance. After hot-pressing, the splices require about 24 to 48 hours to attain their maximum physical properties.

### Flexing of Coated Abrasives

Since coated abrasives are composed of a substrate coated with grain and bonded with a thermoset make and size resin system, such as phenolic or urea-formaldehyde, they tend to be very stiff. *Flexing* is used as a means of imparting various levels of flexibility or conformity to coated products. Flexing causes the coated material to break up, forming many small islands separated by controlled cracks in the bond which act as hinges, enabling the coated abrasive to flex, without dislodging the very stiff and brittle thermosetting resin systems used to make the product. A flexible bond system might satisfy the flexibility requirements but would not have sufficient heat resistance to be effective in many applications. Also, flexible adhesives generally lack the support for the abrasive grit to function aggressively.

### PSA Products

Pressure sensitive adhesives (PSAs) are used extensively to manufacture a special form of

disks and sheets known as PSA-backed products. These coated abrasive products have their backings coated with a PSA, which enables the disks or sheets to adhere to various backup pads without the use of any mechanical means. These adhesives have medium to high tack properties, meaning that they develop a bond immediately upon being applied to another surface with low pressure.

PSA systems include hot-melt, emulsion, solvent-based, and radiation-curable types. Hot melt and radiation systems are 100% solids and require no solvents, thus eliminating the need for devolatilization or solvent recovery systems.

### Markets

There are many market areas in which coated abrasives are used: automotive, industrial metals and fabricators, sporting goods, wood, retail, furniture, aerospace and transportation, just to name a few. For example, the planer belt markets utilize coated abrasive belts to plane rough lumber down to finished size, instead of traditional knife planers. The advantages of abrasives are that they can cut faster, last longer than knives, and are not as sensitive to being damaged by nails or hard items sometimes found in boards.

Today more and more coated products are being employed in industry to shape products as well as finish them. In the automotive markets, coated products serve to finish cars and trucks during manufacturing, as well as to re-

pair body damage in used vehicles. The wood industry is an excellent example of their use in shaping and finishing.

### Machine Methods

Coated abrasives are used on a wide range of different machines. Machine applications can be classified by how the workpiece is fed into the unit or by the type (shape) of abrasive. Machines vary from hand-held sanders to disk grinders, platen grinders, backstand, semiautomatic, and automatic grinding machines. In addition, there are through-feed machines and computerized gantry grinders for cleaning up large metal alloy plates. Coated abrasives can also be utilized on computerized numerically controlled machines for abrasive machining, sophisticated metal parts.

In many applications, coated products can remove material faster, cooler, and at a lower cost, while providing a better finish than other methods of material processing. Coated abrasive products are in existence today because of their unique ability brought about through combinations of abrasives, backings, and adhesive systems.

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# Adhesives for Building Construction

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Glues and sealants have been used in construction since Biblical times; but the synthetic adhesives achieved prominence only after World War II. Even in recent decades, however, changes have been dictated by new adhesive materials and new building materials.

Today, many types of adhesives are in use throughout industry, including the construction industry. Some adhesives require sophisticated application techniques while others can be put in place by trowel, brush, spray, or spot application. This chapter will concentrate on the latter, since most construction applications are carried out at the job site, or at best under rather nontechnical factory applications. Thus in this chapter we will be looking at the factors involved in selecting an adhesive for a particular application, whether it be under factory controlled conditions, by the builder at the job site, or even by the novice do-it-yourselfer.

Areas to be examined where adhesives are commonly used include a variety of materials for floors, subfloors, walls, and ceilings. In addition, we will look at the match between adhesives, construction materials, and substrate to which they will be bonded. Toward the end of the chapter we shall seek to determine why adhesives sometimes do not perform well. In short, this chapter will take an elementary and practical approach to the use of adhesives in construction, leaving the more technical considerations to other chapters in this book.

## BASIC CONSIDERATIONS IN ADHESIVE SELECTION

Selection of an adhesive starts with the answers to five basic questions:

1. *What do we want the adhesive to do for us?* Start by listing all of the requirements expected of the adhesive formulation: the drying time, the ultimate strength needed in the bonded assembly, the years of service expected, the conditions to which the bonded assembly will be subjected, etc.
2. *Is it reasonable or practical to expect all of our basic requirements to be fulfilled by an adhesive formulation?* For example, most adhesives will not perform satisfactorily when subjected to constant submersion under water. Neither will most of the adhesives encountered in the construction industry perform continuously at extremely high temperatures in excess of 300 or 400°F. It is necessary to write down all the factors which, although desirable, could be sacrificed if necessary.
3. *Will you be limited by available equipment, plant layout, production requirements, construction design, special job site tools, etc. in adhesive selection?*
4. *Will insurance rates, local building codes, OSHA, or other government agencies restrict your adhesive selection?*

5. *What effect will the cost of the adhesive formulation, the necessary special equipment required, alterations in construction design, etc. have in the initial selection of a suitable formulation?*

The answers to these basic questions will help narrow the vast field of available formulations to those several to be evaluated further according to (1) application, (2) performance, and (3) cost.

## APPLICATION

Here the main considerations are:

1. *Nature of the substrate and the materials being bonded.* What is the texture of the surfaces—are they smooth, rough, uneven, out of plumb, etc.? A surface that is relatively uneven cannot be bonded to a very smooth surface with a low viscosity adhesive. If one must bridge certain irregularities that are quite common in construction, then heavier viscosity formulations are needed.

The surfaces being bonded may not be dusty, dirty, oily, greasy or wet. The strength of the bonded assembly will never be any greater than the weakest link. When a piece of wood is covered with sawdust, if it is bonded to a concrete substrate, the application is doomed to failure at the sawdust layer.

The adhesive must be compatible with the surfaces being bonded. Polystyrene foam is attacked by some solvent based adhesives. Also, plasticizers can migrate between adhesive and vinyls, or other plastic substrates.

It is important also to consider the internal strengths of the materials being bonded. Most wood fractures internally at shear strengths of 200–400 psi. Thus it makes no sense to select an adhesive that would develop shear strengths of 1000 psi or more. The bond between a low density blanket-type fiberglass and a concrete or metal surface need be no stronger than the bond holding the glass fibers together.

2. *Porosity of the surfaces.* Most adhesives must depend on the release of either a solvent or water to accomplish drying and setup of the glue line. Such adhesives

cannot be used to bond two nonporous surfaces. To bond two nonporous surfaces, one must consider a product that can be predried and perform either as a contact-type cement or a pressure-sensitive adhesive. Other alternatives are catalytically cured systems and hot melts.

The degree of porosity of the substrates will also have a great effect on the drying rate. Both wood and gypsum wallboard are porous, but the drying time will generally be more rapid on the more porous gypsum wallboard.

Some applications may depend on the absorption or penetration of the adhesives into some of the pores of the materials being bonded. An extreme example is a paper honeycomb, where the pores are quite large and deep. The adhesive bed must be sufficiently thick to bond to the edges and sides of the honeycomb pores. Certain types of cinder block also develop superior bonds as there is a degree of absorption or penetration into the surface by the adhesive. Where there is high absorption, the formulation must be sufficiently viscous to assure that there is adequate adhesive at the interfaces.

3. *Preferred systems of application.* The nature of the materials being bonded will many times dictate the preferred method of application. Large surfaces may require a spray or roller coat application. Thin plastics or fabrics may require also a roller or spray. Other applications call for an extrusion, while even others will lend themselves better to trowel, spot, spatula, brush, or other types of application.
4. *Methods available for application.* Any one of the preferred systems of application may have available a number of different systems of varying sophistication. Where an application would require extrusion, for example, a factory controlled situation may dictate a capital expenditure for automatic equipment. At the other end of the scale, the do-it-yourselfer would find a cartridge his best method of extrusion, with a caulking gun. Often an application system already in use can be

adapted to another application, thus reducing cost.

5. *Desired or required viscosity.* One should not attempt to brush a heavy mastic product when the required viscosity is much thinner.
6. *Drying requirements.* The rate of drying, or speed of set, is an important factor, particularly if no auxiliary drying methods are available. In this event one must choose between rapid-drying solvent-based materials versus the slower-drying emulsions and certain other solvent blends. However, if special drying equipment (infrared, forced air, etc.) is available, this, too, will have an effect on the selection. Normally, special drying equipment would be encountered primarily in factory applications rather than on the construction job site.

## PERFORMANCE

In the selection process, applications and performance characteristics are most often considered simultaneously. The following are probably the most commonly used performance criteria.

1. *Minimum tensile, shear or peel strength at specified temperatures.* For the most part, only one of these types of strength evaluation need be considered. There is no need for adhesives to develop strengths far in excess of the internal strength of the weaker of the materials being bonded.
2. *Minimum and maximum service temperatures.* Many formulations perform satisfactorily at temperatures ranging from  $-10^{\circ}\text{F}$  to  $+150^{\circ}\text{F}$ . However, if the application requires performance at temperatures that will exceed  $200^{\circ}\text{F}$ , there is no point in evaluating adhesives designed for performance in these lower ranges. Extreme cold temperatures,  $-30^{\circ}\text{F}$ . and colder, pose an added problem in that many formulations become very brittle at these temperatures. Also a consideration is whether exposure to the upper and lower temperature limits is to be at a sustained rate or intermittent on a cyclical basis.
3. *Glue line resilience required.* On films of fabrics, plastics, etc., a very resilient glue line may be needed. Even on many rigid substrates and adherends, it is desirable to maintain a certain degree of resiliency in the glue line to assure impact resistance. Bonded assemblies of materials that are somewhat mobile and are being moved from place to place also require flexibility and/or resilience of the glue line. Thus, in factory built construction that is moved to other locations, the adhesive should resist racking or other movement that could have an adverse effect on the glue line. There are all degrees of hardness and of resilience.
4. *Resistance to water, moisture, humidity, and light.* In some applications, particularly those with surfaces exposed to the elements, excellent water resistance is desired. Ultraviolet light from sources such as the sun can be very detrimental to some adhesive formulations, particularly SBR and other elastomers.
5. *Resistance to oils, greases, and solvents.* Special formulations may be needed.
6. *Resistance to acids, alkalines, and chemicals in general.* Again, special formulations are available for special environmental conditions.
7. *Aging.* In the construction industry, life expectancy is important. The adhesives industry has come to rely more and more on the oxygen bond test (ASTM-D-572) as an indicator of relative life expectancy of a given formulation. As a general rule, only adhesives that can withstand exposure to 500 hours or more in the conditions encountered in this test procedure should be considered for construction applications. If after 500 hours exposure an adhesive specimen is not hard and brittle, then it can generally be counted on to perform satisfactorily for many years.
8. *Weathering.* Adhesives are generally not subjected to the conditions that are normally considered in weathering tests, since the adhesive is not ordinarily exposed to ultraviolet light. Sealants, however, may well be subjected to ultraviolet, either on the perimeter or through glass



or other transparent or semitransparent surfaces, and then the weathering factor must be considered. Weathering tests involve temperature and humidity cycling, as well as ultraviolet exposure.

9. *Color requirements.* Color may be a factor for a number of reasons, for example, matching the colors of the materials being bonded, preventing adhesive shadows from showing through opaque surfaces, masking excess squeeze-out in inaccessible places such as dark tongue and groove wood joints, and identification.

## COST CONSIDERATIONS

The third major factor of consideration in the initial adhesive selection process is cost. You will notice that references to cost have generally been set aside until last. While of importance in some specialty applications, cost generally is less significant than either application or performance criteria. The factors that most commonly affect cost are the following:

1. *Initial cost.* Unfortunately, the inclination is often to put cost of the material per gallon or per pound before any other consideration. In most cases this can lead to problems. While it certainly must be taken into consideration, the base cost of the adhesive generally is not one of the initial selection factors that is evaluated, and would come further down the line. It will again go hand in hand with application and performance considerations, but generally will follow them in order of consideration.
2. *Performance requirements.* Cost will be greatly affected by the performance requirements. In most cases as these requirements are raised, so will be the cost of the adhesive. Performance will generally have a much greater influence on cost than any other consideration.
3. *Service requirements.* Technical expertise, experience in the industry, and reputation for quality and service should be prime considerations in selection of an adhesive supplier and formulation. While lower cost adhesives or reduced usage

will reduce initial costs, technical service from the manufacturer is much more cost effective, greatly reducing the chance of future adhesive problems, which can be extremely costly in time, replacement, call-backs, and loss of business.

4. *Application consideration.* There are, of course, certain applications that require specific types of adhesive. Again, available equipment may limit adhesive choice, and special adhesives can be very expensive. Generally speaking, however, the performance requirements are much more rigid than application requirements.
5. *Coverage.* There are a number of factors that affect coverage, hence cost. Generally speaking, lower viscosity adhesive formulations will yield higher coverages than the heavier viscosity formulations, thus reducing the cost per square foot. However, the nature of the application may be such that a lower viscosity adhesive is unsuitable.

Application techniques and methods will also have a great effect on coverage, as will design of the application system, its efficiency, and cleanliness.

As pointed out before, the nature of the materials being bonded, the demand placed upon adhesive performance and the application methods used or available all combine in the initial selection process. These factors dictate the type adhesives that will be candidates for your application. It is then that cost factors enter into consideration and efficient coverage will play its role.

## Coverage Data

Mastic type formulations are generally applied by either an extrusion or by some type of trowel application or variation thereof. Extrusions can either be with the utilization of some type of automatic equipment or by common cartridge gun extrusion.

The data in Table 1 may be of help in estimating coverage of mastics. The figures are modified by other variables that affect coverage such as inconsistencies or human error in hand applications, temperatures at point of application, efficiency of application systems, clean-

Table 1. Volume of Extruded Bead Length vs. Bead Size.

Volume	Bead Size, in. diam.				
	$\frac{1}{8}$ "	$\frac{3}{16}$ "	$\frac{1}{4}$ "	$\frac{5}{16}$ "	$\frac{3}{8}$ "
Small Cartridge (10 fl. oz.)	123 ft	54 ft	30½ ft	19½ ft	13½ ft
Small cartridge (10.5 fl. oz.)	129 ft	57 ft	32 ft	20½ ft	14 ft
Large cartridge (29 fl. oz.)	355 ft	158 ft	89 ft	57 ft	39 ft
1 U.S. gallon (128 fl. oz.)	1,569 ft	597 ft	392 ft	251 ft	174 ft
5 gallons (Pail)	7,845 ft	3,485 ft	1,960 ft	1,255 ft	870 ft
52 gallons (Drum)	81,588 ft	36,244 ft	20,384 ft	13,052 ft	9,048 ft

In approximate figures, 1000 lineal feet of extruded adhesive bead will require:

- $\frac{3}{4}$  gallon at  $\frac{1}{8}$ " diameter bead
- 2½ gallons at  $\frac{1}{4}$ " diameter bead
- 5½ gallons at  $\frac{3}{8}$ " diameter bead

liness of the system, etc. Glue patterns are shown in Table 2.

Trowel Coverage

Hand trowels change coverage with build up of dried adhesive on the trowel edge, with the angle at which the trowel is held, and with wear in contact with an abrasive surface such as concrete for a prolonged period of time. Table 3, based on a clean trowel held at an approximate 45° angle, shows typical coverage. See Fig. 1.

Other Types of Applications and Their Coverage

Here again, there are so many variables that it is most difficult to state precise coverage figures. Since coverage is greatly affected on certain applications by the viscosity of the adhesive, the solids, the cohesion within the material, etc., an arbitrary viscosity of 8,000–10,000 cps has been selected in Table 4. Typ-

Table 3. Trowel Coverages.

Trowel	Approx. Coverage (sq. ft per gal.)
Square notch trowel (Notches $\frac{3}{16}$ " wide $\times$ $\frac{1}{8}$ " deep $\times$ $\frac{5}{16}$ " o.c.)	34
Sawtooth trowel (Notches $\frac{3}{16}$ " wide $\times$ $\frac{1}{8}$ " deep $\times$ $\frac{3}{16}$ " o.c.)	54
Serrated V-notch trowel (Notches $\frac{3}{16}$ " wide $\times$ $\frac{1}{8}$ " deep $\times$ $\frac{1}{2}$ " o.c.)	66
(Notches $\frac{3}{16}$ " wide $\times$ $\frac{3}{16}$ " deep $\times$ $\frac{7}{16}$ " o.c.)	41
(Notches $\frac{3}{16}$ " wide $\times$ $\frac{3}{16}$ " deep $\times$ $\frac{9}{16}$ " o.c.)	54

ical solids content of a product of this type would be in the range of 30–50%.

COMMON ADHESIVE APPLICATIONS IN THE CONSTRUCTION INDUSTRY

Table 5 shows some of the most widely available types of adhesive and the substrates and facing surfaces on which they are commonly used. Do not rely on this table alone. Use it in conjunction with a performance, application, and cost analysis.

Table 6 shows some of the general characteristics of the most commonly used adhesives by type, and can be particularly useful in the

Table 2.

### Glue patterns typical on 4'x8' panels, flat lamination

The diagram illustrates five different glue patterns for 4'x8' panels. Pattern 1 shows a 3' bead and 3' skip. Pattern 2 shows vertical lines. Pattern 3 shows a diagonal cross. Pattern 4 shows horizontal lines. Pattern 5 shows a diagonal cross with horizontal lines.

Bead length in ft.	32'	40'	42'	44'	50½'
Rqd. oz. @ ¼" bead	2.6	3.3	3.4	3.6	4.1
Rqd. oz. @ ½" bead	10.5	13.1	13.7	14.4	16.5
Rqd. oz. @ ¾" bead	23.5	29.4	30.9	32.3	37.1

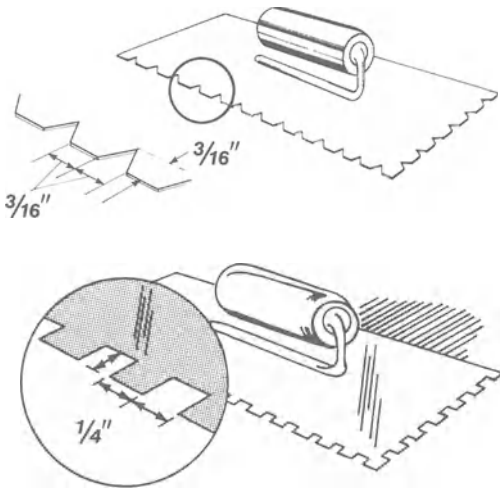


Fig. 1. (Top) Typical V-notch spreader used with tile-board adhesives. (Bottom) Typical notched trowel used to apply floor mastic.

evaluation of the performance criteria of a particular formulation. Both Table 5 and Table 6 are quite general but can assist in zeroing in on the best possible formulation.

## FLOORING

The first major category of construction elements to be examined is flooring. Among the major choices for floor coverings are wood, resilient surfaces, rigid surfaces (ceramic tile, slate, and brick), and soft fabric materials such as carpeting. All of these floor coverings can be easily installed with the proper adhesives. Before discussing some of them more specifically, however, we need to address two very important subjects. One is the use of the American Plywood Association Glued Floor System in basic construction work and the other is the

treatment and/or preparation of the subfloors prior to installing any type flooring over them.

In most remodeling or refurbishing jobs around the home, the existing floor will act as the subfloor for the new flooring material. However, in conventional stick-type construction, or the finishing of an attic, basement, or garage, or when rooms are added to existing construction, a subfloor of some type must be installed to receive the finished flooring material. In the addition of rooms or new construction work, adhesives can play a very important part.

Since the mid-1960s the American Plywood Association has been carrying on an intensive program to perfect subfloor systems that would improve floor quality and performance while using less material. The APA's present system is based on recently developed gluing techniques and adhesives that firmly and permanently secure the structural plywood underlayment to wood joists. The resulting bond is so strong that floor and joist behave as integral T-beam units. This combination of joist, plywood and adhesive increases stiffness when compared with conventional floor construction. For instance, stiffness of the joist is increased significantly (about 25% with 2" × 8" joist and  $\frac{5}{8}$ " plywood) when a single layer of plywood underlayment is glued to the framing joist. Gluing the tongue and groove joint between panels approximately doubles the increase in stiffness (to about 50% in the case mentioned). Thus, glued floors not only deflect less under traffic but tests show better resistance to long term deflection than nailed-only floors. There are many other benefits to the use of the APA Glued Floor System, not the least of which is the virtual elimination of squeaks in the floors. Extensive testing undertaken by the APA also indicates that the glued floor system will provide many economies while increasing and improving the structural performance of the entire unit. The increased spacing to 24" on center from conventional 16" floor joist will save nearly one-third of the framing members required and result in higher strengths than conventional nailing on 16" spacing. Tests have also found that spans can be increased considerably by the various sized framing members. The design of a typical

**Table 4. Spray, Brush and Roller Application.**

Spray equipment used was	
Binks #62 gun/#365	
needle/67 pb air cap. 66	
Fluid tip/55 lb. line pressure and 8 lb. cup pressure.	250-350 sq. ft/gal
Brush coverage—medium coat	175-225 sq. ft/gal
Roller coverage—Carpet	
Stipple Roller	300-350 sq. ft/gal

Table 5. General Selection Practices by Type of Adhesive.

Facing Surfaces	Substrates (Back Up Surfaces)									
	Concrete Cinder Block	Concrete (Poured)	Gypsum Board	Gypsum Plaster	Hardboard	Metal	Particle Board	Plywood	Wood	
Brick Veneer	D,b,e	D,b,e	B,D,f,h,m	B,D,f,h,m	B,D,f,h,m	D,b,e,k	B,D,f,h,m	B,D,f,h,m	B,D,f,h,m	
Carpet	B,f,h,m	B,F,H,M	B,f,h,m	B,f,h,m	B,f,h,m	B,f,h,m	B,F,H,M	B,F,H,M	B,F,H,M	
Ceramic, Slate	B,c	B,c,f	B,F,c,h	B,F,c,h	B,F,c,h	B,c	B,F,c,h	B,F,c,h	B,F,c,h	
Quarry Tile										
Chalkboard &	B,d	B,d,f,h,m	B,d,f,h,m	B,d,f,h,m	B,d,f,h,m	B,d,f,h,m	B,d,f,h,m	B,d,f,h,m	B,d,f,h,m	
Cork										
Cove Base	D,L,b,h	D,L,b,h	D,L,b,h	D,L,b,h	D,L,b,h	D,b,h	D,L,b,h	D,L,b,h	D,L,b,h	
Cultured	B,D	B,D	B,D,h	B,D,h	B,D,h	B,D	B,D,h	B,D,h	B,D,h	
Marble										
Furring Strips	B,D	B,D	B,D,f,m	B,D,f,m	B,D,f,m	B,D	B,D,f,m	B,D,f,m	B,D,f,m	
Gypsum	B,D	B,D,f,m	B,D,a,f,m	B,D,f,m	B,D,a,f,m	B,D	B,D,a,f,m	B,D,a,f,m	B,D,a,f,m	
Wallboard										
Hardboard	B,D	B,D,f,m	B,D,a,f,m	B,D,a,f,m	B,D,a,f,m	B,D	B,D,a,f,m	B,D,a,f,m	B,D,a,f,m	
Paneling										
Insulation	B,D	B,D	B,D,f,h,m	B,D	B,D,f,h,m	B,D	B,D,f,h,m	B,D,f,h,m	B,D,f,h,m	
Board										
Metals	B,D,k	B,D,c,k	B,D,h,k,m	B,D,h,k,m	B,D,h,k,m	B,C,D,E,K	B,D,h,k,m	B,D,h,k,m	B,D,h,k,m	
Marble	B,D,k	B,D,k	B,D,k	B,D,k	B,D,k	B,D,c,k	B,D,k	B,D,k	B,D,k	
Wood Parquet	B,D,h,k	A,B,d,h,k	A,B,d,h,k	B,D,h,k	A,B,d,h,k	B,D,c,e,h,k	A,B,d,h,k	A,B,d,h,k	A,B,d,h,k	
Plastic	b,c,d,e	b,c,d,e	D,E,c,b	D,E,c,b	D,E,b,c	b,c,d,e	A,D,E,b,c	A,D,E,b,c	A,D,E,b,c	
Laminates										
Plywood &	B,a,d,f,m	B,a,d,f,m	A,B,d,f,m	A,B,d,f,m	A,B,d,f,m	B,D,f,m	A,B,d,f,m	A,B,d,f,m	A,B,d,f,m	
Paneling										
Polystyrene	A,B,F,H,M	A,B,F,H,M	A,B,F,H,M	A,B,F,H,M	A,B,F,H,M	B,F,H,M	A,B,F,H,M	A,B,F,H,M	A,B,F,H,M	
Foams										
Polyurethane	A,B,D,F,	A,B,D,F,	A,B,D,F,	A,B,D,F,	A,B,D,F,	B,D,h	A,B,D,F,	A,B,D,F,	A,B,D,F,	
Foams	H,M	H,M	H,M	H,M	H,M		H,M	H,M	H,M	
Subflooring	B,D	B,D	B,D,a,m	B,D,a,m	B,D,a,m	B,D	B,D,a,m	B,D,a,m	B,D,a,m	
Tileboard	B	B	B,l	B,l	B,l	B,d	B,l	B,l	B,l	
(Wallboard)										
Plastic Tub &										
Showers	B	B	B,f,h,m	B,f,h,m	B,f,h,m	B	B,f,h,m	B,f,h,m	B,f,h,m	
Vinyl Floor										
Materials	F,h,m	F,h,m	F,h,m	F,h,m	F,h,m	F,h,m	F,h,m	F,h,m	F,h,m	
Wood Flooring,										
Strip & Plank	B,c,d,k	B,c,d,k	B,d,k	B,d,k	B,d,k	B,d,k	B,d,k	B,d,k	B,d,k	
Wood/Plywood	B,D,k	B,D,c,f,h,k	A,B,F,d,h,	A,B,F,d,h,	A,B,F,I,J,	B,D,c,e,k	A,B,F,I,J,M,	A,B,F,I,J,M,	A,B,F,I,J,M,	
			k,m	k,m	M,d,h,k		d,g,h,k	d,g,h,k	d,g,h,k	

## ADHESIVE TYPES:

- a. Polyvinyl Acetate  
b. SBR—(Solvent)  
c. Epoxies  
d. Neoprene rubber (Solvent)  
e. Nitrile (Solvent)  
f. Latex emulsions  
g. Hot Melts  
h. Acrylics (Latex)  
i. Animal Glues  
j. Resorcinol  
k. Polyurethanes  
l. Resin/Rosin Based  
m. Ethylene/Vinyl Acetate  
Capital Letters—Most commonly used  
Lower Case Letters—May also be used

Table 6. General Characteristics of Adhesive Types.

Materials	Systems of Curing or "Setting"	Methods of Application	Application Temperature °F	Temperature Service Range In Degrees F (a)	Shear Strength Range at 70 Deg. F In Psi (b)	Stability of Adhesive Types for Various Surface Conditions							
						Resistance to Water	Resistance to Weathering	Resistance to Alkalies, Chemicals	Initial Tack or Wet Strength	Cohesive Strength (Dry)	Porous to Porous	Porous to Non-porous	Non-porous to Non-porous
Polyvinyl Acetate	Water Evap., Heat, Pressure	Brush, Spray, Roller Flow	35° to 100°	-20° to 180°	100 - 4000	G	P-E	P-F	P-F	E	E	G	P
SBR (Butadiene Rubber)	Solvent Evap.	Brush, Spray, Roller, Ext.	0° to 120°	-20° to 200°	50 - 700	P-F	F-G	P-F	F-G	F-G	G	G	G
Epoxies	"Catalyzed" Curing Agents	Brush, Flow Roller	40° to 100°	-20° to 350°	50 - 5000	E	G	G-E	F-G	E	G	E	E
Neoprene Rubber	Solvent Evap., Heat	Brush, Spray, Roller, Extrusion	0° to 120°	-40° to 300°	20 - 500	G-E	G-E	G	G-E	G-E	G	G	E
Nitrile Rubber	Solv. Evap., Heat	Brush, Spray, Roller, Extrusion	0° to 120°	-40° to 300°	20 - 500	E	G-E	G	G-E	G	G	G	E
Latex Emulsions	Water Evap.	Brush, Spray, Roller, Ext., Trowel	40° to 100°	-30° to 200°	50 - 300	P-F	P-G	P-F	P-F	F-G	E	G	P
Hot Melts	Heat Loss	Brush, Flow Extrusion	140° to 350°	-20° to Melt	20 - 500	P-F	G	F-G	F-G	F-G	G	G	G
Acrylics (Latex)	Water Release or X-link	Brush Flow Ext., Trowel	0° to 100°	-40° to 400°	10 - 300	F-G	F-G	F-G	P-G	F-G	G-E	F-E	F-E
Animal Glues	Water Evap. or Heat loss	Spray Brush, Flow Roller	70°	-20° to 200°	500 - 4000	G	P	P-F	F	P-F	E	E	P
Resorcinol	Water Release, Heat Pressure	Brush, Flow Roller	70°	-20° to 250	1000 - 4000	G	E	G	F	E	E	G	P
Polyurethanes	Solv. or Water Rel., X-link	Brush, flow Ext., Spray	40° to 120°	-40° to 300°	20 - 700	F-G	F-E	G	F-G	F-G	G	G	G
Resin/Rosin	Solvent Release	Trowel Extrusion	40° to 100°	0° to 180°	20 - 200	P-F	F-G	P	G-E	G-E	G	G	G
Eva Latex	Water Evap.	Brush, flow Ext., Spray Trowel	35° to 100°	-20° to 200°	50 - 500	F-G	F-G	F-G	P-G	F-G	G	G	F-G

Notes: (a) Dependent on nature of materials being bonded such as thermal conductivity, thickness, required strengths at given temperatures, etc.

(b) Varies with type of materials being bonded, method of application, thickness of bond line. etc: E = Excellent; G = Good; F = Fair P = Poor

subfloor system using the American Plywood Association Glued Floor System is shown in Fig. 2.

From an adhesive point of view, the APA specification is quite strict in spelling out the performance characteristics of adhesives for use in this system. As a matter of fact both the APA Glued Floor System and HUD-FHA, in their Use of Materials Bulletin #60, require independent outside laboratory testing for the conformance of these adhesives to AFG-01 carried out with field samples of adhesives procured at random. This is one of the very few specifications in the construction industry that has built-in quality assurance for the user. It is highly recommended that the APA Glued Floor System be thoroughly investigated and considered in basic construction and remodeling work.

### Treatment of Subfloors

There are many existing subfloors or substrates that can be used as surfaces for applying finished flooring materials. However, these surfaces often may also be the source of serious problems if they are not properly addressed and treated. Before attempting to install any flooring material, the subfloor should be thoroughly examined to make certain that it will provide a suitable and satisfactory base.

**Poured Concrete.** This is probably one of the most common surfaces to which modern day flooring materials are bonded. One of the most common problems with concrete is the

moisture conditions that may exist underneath the slab. Just because a slab is above grade, it is not necessarily totally moisture free. In new construction the builder/contractor should always insist that some form of plastic vapor barrier with proper drainage be used underneath the slab prior to pouring of the concrete. While wet surfaces on concrete may not necessarily be harmful to the adhesive, they may be quite detrimental to the flooring material itself.

A practical test to determine the presence of moisture in a concrete slab, whether it is new or has been down for a number of years, is the following. A piece of polyethylene sheet approximately 36" square should be taped to a clean surface of the slab with a standard duct tape applied completely around the perimeter. If moisture is present in the slab, it will generally show up within 48 hours as condensation underneath the polyethylene film. In this event, one should thoroughly check out the source of the moisture and attempt to eliminate it prior to installing any type of flooring material.

It also stands to reason that it will be most difficult to achieve a satisfactory bond on concrete that is loose, flaky, or spalled in any way. Occasionally, curing agents have been used in the concrete that may have a tendency to rise to the surface and create salts that are most difficult to bond to. In this event these salts should be removed before attempting to adhere any type flooring material. All cracks or rough areas on the concrete should be patched prior to proceeding with flooring installations. Naturally the surface should also be free of any dust, dirt,

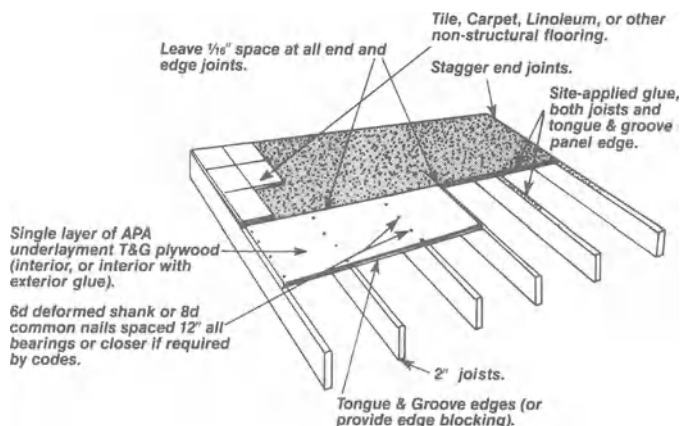


Fig. 2. APA glued floor system (Courtesy of American Plywood Association).

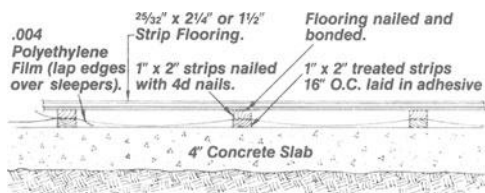


Fig. 3. Laying strip floors over a concrete slab.

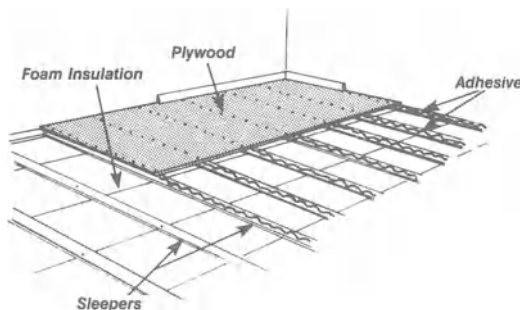


Fig. 4. Insulated floor over a concrete slab.

oil, or grease prior to installing finished flooring.

Concrete slabs are occasionally damp or have some moisture content or may be exposed to moisture conditions. A system to provide a vapor barrier when wood floors are put down over concrete is shown in Fig. 3. The sleepers may be bonded to the concrete slab with construction type adhesives. Occasionally asphalt cutbacks are also used for this purpose.

In the event that it is desirable to insulate the floor underneath a plywood subfloor, foam insulation can be placed between sleepers that have been installed over slabs, as shown in Fig. 4, with the aid of either construction adhesives or asphalt cutbacks.

**Wood Subfloors.** While plywood is still probably one of the most common subfloor surfaces made from wood, we are beginning to see other types of composition subfloors: particle board, flake board, wafer board, etc. Most of these types of surfaces are treated like plywood. Large gaps between the subfloor and the floor should be filled with a suitable wood filler. All nails must be flush with the surface and not protruding. Since these subfloors are generally in existence during all other phases of construction, they may accumulate dirt and dust which must be cleaned prior to making any further

finished flooring installations. Flooring is generally the last piece of finish work to be done on any construction project; thus the subfloors take much abuse during the construction process and need attention to make certain they will be receptive to a good bond.

**Existing Floor Surfaces.** Often it is desirable to apply a new flooring material over an older existing floor. In most cases this can be accomplished, provided the potential problems are addressed. For example, on existing vinyl tile or vinyl sheet floors there is often a buildup of wax and dirt that would interfere with bonding. These floors should be stripped of all wax and dirt. One should also be certain that these existing floors are well bonded and have not delaminated from the subfloor with the old adhesive.

When old existing floors are removed, all traces of old adhesives on the subfloor must be removed. Often these older adhesives are not compatible with newer adhesives that would be used to put down modern floors; there can be a migration of plasticizers between the two adhesives, resulting in a glue line that will never set up or develop a strong bond.

Questions regarding the treatment of these subfloors can be answered by the manufacturers of the flooring material and the adhesive as well as the flooring system dealer or distributor.

## Floors

**Wood Floors.** Wood floors probably were first installed in the mid-11th Century, and have been a leading flooring material ever since. Today both hardwoods such as oak, birch, beech, and maple, and softwoods such as pine and fir are used for wood flooring. A number of different types of wood floors are installed with adhesives; among these are solid block parquet, laminated parquet, solid finger block, strip, and plank-type flooring.

Fortunately most of the wood floors installed today utilize a very narrow range of adhesives, which greatly simplifies the selection decision. These are as follows:

1. *Asphalt cutbacks.* Until a few years ago the majority of wood floors installed with

adhesives utilized these asphalt cutback formulations. Unfortunately, their flammability posed an extreme hazard to the workmen as well as the structural elements during installation. While there still are some examples of this type material being used today, the liability that the user is exposed to has virtually eliminated this as a selection. The chief reason for their use was basically economic, in that the asphalt materials were generally quite low in cost. However, they normally did not develop the strengths that were desired, and this, coupled with the hazard involved, prompted most users to switch to the nonflammable, chlorinated solvent SBR (butadiene-styrene rubber) formulations.

2. *Chlorinated solvent systems.* Most adhesive-installed wood flooring today utilizes this type of material. They are nonflammable because they utilize 1,1,1-trichloroethane or other chlorinated solvent with a base such as butadiene-styrene rubber. High strengths are achieved, yet the material remains sufficiently resilient to allow normal expansion and contraction of the flooring and the substrates without delamination. In virtually all cases the adhesives are applied by notched trowel.
3. *Polyvinyl acetate systems.* It is not uncommon today for the finger block flooring materials, particularly those that are unfinished, to be installed with a form of PVA adhesive. While these products are water based materials, they dry extremely rapidly and will normally not cause any warpage problems in the finger block types of flooring. Some of the formulations will dry sufficiently within three to five hours to allow the installer to begin sanding operations to smooth the surface prior to finishing. Generally, unfinished finger block installed with polyvinyl acetate adhesives requires the skill of an experienced contractor.
4. *Epoxy resins.* Installations are occasionally made with epoxies, but, the strengths these adhesives develop generally far ex-

ceed the internal strengths of the wood, and they are unnecessarily expensive as well as difficult to use. Furthermore, there have been a number of failures because the bond strengths were so high that delamination occurred when the floor contracted and expanded and there was no accommodating resiliency in the glue line.

It should be always kept in mind that wood and water are inimical. There should never be any attempt made to install any type wood flooring if water or moisture is present. The presence of moisture has most probably been the single largest problem with installing wood flooring.

**Resilient Flooring.** Practicality, convenience, ease of application, and long wear are a few of the reasons why resilient flooring continues to be one of the most popular choices of homeowners everywhere. With the tremendous variety of materials, designs, and colors available it is possible to create virtually any floor scheme that strikes the fancy.

Resilient floors generally are manufactured in two basic types: sheet material and tiles. The sheet materials are generally available in continuous rolls up to 12' and larger widths. One of the key advantages of sheet flooring is the huge reduction in seams in the finished floor; another is the beautiful wall-to-wall sweep of color and design. These sheet or roll goods of resilient materials, including carpeting, are installed with latex emulsion-type adhesives, which are normally troweled over larger areas and remain open long enough to permit shifting and adjustment of the roll goods into position.

It is important that the recommendations and instructions of both the flooring manufacturer and the adhesive manufacturer be followed. Adhesives must be of good quality to insure a long lasting installation. Certain types of foams present in foam-backed sheet goods may not be compatible with some of the adhesives that are generally sold for roll goods application. In the event a particular piece of sheet goods or carpeting is foam backed, one should determine absolutely that the adhesive used is compatible with these foams by means of a test on scrap.



Also, the recommended notched trowel for the installation must be used to achieve the proper laydown.

**Resilient Tile.** These tiles are commonly based on vinyls. Good quality multipurpose latex emulsion adhesives very similar to those used for roll goods are also satisfactory for resilient tile installations. However, since most of these resilient tiles are in either 9" × 9" or 12" × 12" pieces, they can also be installed with lower-viscosity pressure-sensitive adhesives. Some of these are referred to in the trade as *clear, thin spread adhesive*. These adhesives can be applied by either a brush, trowel or roller coat over rather large areas. Generally they are allowed to dry to a point where they become pressure sensitive; then the tile is placed into position in the adhesive bed, and bond is immediate. These pressure-sensitive formulations have exceptionally high green grab, so that one can walk on the floor during and immediately after their installation. For the do-it-yourselfer, the installation of vinyl tiles with these low-viscosity, clear, thin spread adhesives is virtually foolproof, even for the most inexperienced individual.<sup>1</sup>

A common finishing item for various types of flooring are vinyl and rubber cove base trims. Generally, resin-type adhesives are used for these cove bases, extruded in parallel strips approximately 1½" to 2" apart along the back of cove base. Alternatively, cove base can be installed very efficiently with neoprene contact cements. The cove base is first put into position without any adhesive, and a light pencil mark made along the top edge of the cove onto the wall surface. The neoprene contact cement is then brushed in the space below the pencil mark as well as on the back side of the vinyl or rubber cove base, the solvent is allowed to evaporate, then cove is pressed into position for immediate bond.

Wood trim pieces are sometimes placed on hard wall surfaces such as poured concrete or concrete block. These wood moldings can be bonded with SBR solvent-based adhesive, extruded from cartridge onto the back of the cove base and then pressed into position. A common form of this adhesive is referred to as *construction adhesive*.

**Rigid or Hard Material Flooring.** Ceramic tile, ceramic mosaic tile, quarry tile, slate, and marble are all examples of the more rigid flooring materials. All can be installed with adhesives. The subfloor or substrate is likely to be either a concrete slab or plywood or similar composition wood material. Once again it is important that these subfloors be clean, dry, and free from dust, dirt, oil, grease, etc. Most installations of these rigid substrates utilize similar adhesives.

**Ceramic or Ceramic Mosaic Tile.** Ceramic tile is thin compared to other rigid flooring materials and calls for smaller notched trowels for spreading the adhesive on the substrate. Excessive amounts of adhesive should be avoided and the tile should not be moved around after it has been imbedded in the adhesive. These practices tend to cause the adhesive to push up into the joints and make it difficult if not impossible to properly grout the tile after the adhesive has set. Solvent-based SBR and nitrile formulations as well as SBR latex emulsions are commonly used. It is important to select a formulation that dries quite rapidly and that will enable grouting the tile within a 24–48 hour period. This requirement favors solvent systems over the slower drying latex emulsions. Since the grouting process involves pressure on the tile, for example by standing on it, it is important that the adhesive develop strong bonds quickly to avoid shifting of the tiles during grouting.

**Quarry Tile.** Quarry tile may also be installed with adhesives, and because of its thickness and size, calls for larger notched trowels for spreading the adhesive. Here again the adhesive must develop its strength quite rapidly to permit grouting of joints. The selection of grouts with adhesive-installed flooring systems is critical. These floors tend to have some degree of movement and deflection. Therefore, rigid setting grouts will have a tendency to crack out of the joints. It is recommended on adhesive-installed floors that the grouts utilize a latex base in order to provide resiliency.

**Gauged Slate.** Slate is generally available either gauged or ungauged. Most slate is cut into random pattern designs and installed in this fashion. Adhesive installations of slate can only

be accomplished with *gauged slate*, which has been uniformly sized by grinding down to standard thicknesses. Ungauged slate is generally installed on a thick bed of portland cement rather than adhesives, because it is quite uneven. In installing gauged slate, the grout must again have a resilient base to allow for movement and deflection.

**Marble.** Adhesives for marble are similar to those for other rigid flooring materials. However, there is another potential consideration with marble: the translucency of some marbles may permit dark-colored adhesives to show through. Therefore, the adhesive must be rather light in color.

There will be from time to time new rigid flooring materials. Usually they will be bonded with an elastomer, solvent-based SBR (butadiene-styrene rubber). However, it is not uncommon to find some emulsions (water based systems) that are satisfactory. Some of the larger rigid flooring pieces may have a degree of warpage. Therefore, it becomes imperative that the correct notched trowel be used to provide the optimum thickness of adhesive between the substrate and the flooring material.

## WALL AND CEILING ELEMENTS

The use of adhesives for installing wall materials has grown immensely since the end of World War II. A rather wide variety of adhesives are designed for the various wall coverings according to the specific requirements of each.

On poured concrete walls or masonry walls, it is becoming common to utilize some form of insulation such as polystyrene foam, polyurethane foam, or fiberglass before installing the finished wall covering. Polystyrene foam may require special adhesive formulations that do not attack it.

Furring strips also may be installed directly to concrete and masonry walls to provide a backup surface for the installation of finished wall covering. Such applications on furring strips generally utilize a high quality construction adhesive.

Gypsum wallboard is quite frequently installed with adhesives direct to furring strips or studs. This wall covering can provide either a

finished surface or an excellent backup surface for other wall covering products. Adhesive-installed gypsum wallboard has many advantages, to be discussed later. Construction adhesives or panel-type adhesives are most frequently used, many specifically labeled for gypsum wallboard installations.

Paneling is one of the most common wall covering materials applied with adhesives. Prefinished plywoods, solid woods, and prefinished hardwood are but a few types of paneling. Some of these require specific adhesive formulations, while others can utilize the general panel adhesives. Some forms of prefinished plywood and hardboards are applied directly to gypsum wallboard surfaces using adhesives troweled over the entire surface of the paneling. The adhesives used must have longer working times than are normally found in cartridge extrusions of panel adhesives. These trowel-type products are called *tileboard adhesive* and are suitable not only for prefinished hardboard but also for other types of paneling.

It is not uncommon to find flooring materials used as wall covering, for example, wood parquet flooring and carpeting. They require different adhesives from those used on floor installations, with sufficient green strength to hold the flooring material in a vertical position.

Ceramic and mosaic tiles also require special adhesives. Latex emulsion formulations are generally used, troweled onto the wall surface prior to the installation of the ceramic or mosaics.

Another unusual type wall covering material is the plastic laminates found on countertops. These are quite commonly installed on wall surfaces for backsplashes. This requires a more viscous adhesive than the contact cements that are normally used on countertop work, because of uneven wall surfaces.

## Backup Surfaces or Substrates for Wall Covering Materials

As with floors, it is important to have acceptable substrates to which to bond the finished wall covering. Many walls are out of plumb and require some type of furring or adjustment in order to be receptive to a plumb finished wall. Other walls may have moisture problems,

dusty or dirty surfaces, or loose, scaly paint that does not provide a good surface to which to apply wall coverings.

#### **Concrete and Masonry-Type Substrates.**

A word of caution about poured concrete walls. Often the forms for making these walls are coated with oils or other mold releases to prevent the concrete from adhering to the form. If these are not removed from the cured concrete wall surface, it will be difficult to get any adhesive to adhere. Therefore, one should be certain that these walls have been thoroughly cleaned and are free from any oils or mold releases. Masonry construction, on the other hand, generally does not utilize oil or mold release materials, but does have a problem of mortar squeezing out from the joints, creating an uneven surface. This can generally be corrected quite easily by thoroughly wire brushing prior to application. In the event moisture is present, steps should be taken to eliminate it from the masonry or concrete walls prior to putting on any other wall covering. If the moisture problem is not addressed prior to the installation of the wall covering, it will most probably persist and worsen as time goes on, providing a very inadequate surface for wall covering installations.

#### **Existing Plaster or Gypsum Wallboard Surfaces.**

On older construction there is a good possibility that there are a number of coats of paint over the surface of the gypsum wall board or plaster. Before any wall covering can be bonded to these surfaces, one must make absolutely certain that the paint is well bonded and that it will not be softened by any ingredient of the adhesive formulation. This generally can be determined by applying some adhesive over the paint in an obscure spot and allowing it to dry for 24 hrs to determine whether it has good bonding properties with the painted surface. It goes without saying that all loose and scaly paint must be removed before an attempt is made to bond anything to the surface.

**Plastic Foams.** It is becoming common to use either rigid polystyrene or polyurethane foam as a backup material for certain types of

wall covering, particularly over exterior masonry or poured concrete walls. Polyurethane foams are generally not harmed by the solvents contained in adhesive formulations commonly used for wall coverings. However, polystyrene foams are very susceptible to attack from solvent-based systems unless the formulation is specifically developed for the installation of polystyrene foams. Therefore, adhesive for the polystyrene foams must be selected cautiously, whether the foam is to be bonded to a substrate or a finished paneling material is to be bonded directly to the foam.

Generally, any uneven substrate or backup surface should be furred out prior to applying additional wall covering, but panel-type adhesives may bridge some minor irregularities.

#### **Types of Adhesive for Wall Coverings**

**Construction Adhesives.** Unfortunately the commercially available adhesives labelled "construction" range in quality from poor to excellent. One way to be assured that the construction adhesive is of acceptable quality is to look for the hallmark on the label that the product is certified to comply with the American Plywood Association's specification AFG-01, a very rigid test.

The label information must be read carefully. Do not assume that a product can be used on polystyrene foams unless this is stated. The label will also indicate if it is satisfactory to use on treated lumber. Some of the treated lumber available today requires special adhesives for good bonding results, but the better quality construction adhesives will perform satisfactorily. Virtually all construction adhesives would be satisfactory for panel installations directly to studs or furring strips. These adhesives are generally available in cartridge containers for extrusion of beads. They have the advantage of bridging framing irregularities. Here again, though, you can not expect miracles on this bridging characteristic and most manufacturers will state on their label the minimum and maximum bead size that should be used.

Many high quality construction adhesives can be used on exterior applications other than wood decks. Many spot applications on surfaces that are normally difficult to secure by

nails or other mechanical fasteners can be serviced by these construction adhesives. Some that are specifically formulated for high temperature work, such as the neoprene-based mastics, are suited for metal building use. However, in roof applications on metal buildings, temperatures become quite severe, even exceeding 200–250°F in the summer.

**Panel Adhesives.** Panel adhesives are generally formulated specifically for the installation of either prefinished plywood paneling or hardboard paneling of some type. They do not have the high performance requirements—either high temperature or high shear strength—of the better construction adhesives. Nevertheless, most panel adhesives used today would actually fracture the wood they are bonded to before they would delaminate internally. They are typically high-viscosity mastics.

**Tileboard Adhesives.** These viscous adhesives are generally applied by a notched trowel spreader. They would be used on large sheets up to 4' × 8' where the entire back of the sheet would be troweled and then placed into position on the existing wall. These adhesives require certain characteristics not normally found in panel adhesives. They must have a long working time in order to avoid the drying out of the mastic too severely before installation; but they still must have an adequate amount of green grab or tack to hold the panel in position when it is placed on the wall. This type of product is used to apply paneling over existing wall surfaces, which must first be suitably treated. Trowels used for these applications should be frequently cleaned to avoid buildup of adhesive on the notches, as this would result in too little adhesive being applied on the surface.

**Foamboard Adhesives.** Foamboard made from polystyrene foam or bead board is very susceptible to solvent attack or solvent etching. Thus many of the available solvent-based construction and panel adhesives are unsatisfactory for the installation of foams. The adhesive under consideration should be tested by placing a bead of adhesive between two pieces of foam overnight, then breaking it apart and inspecting

the area around the adhesive for solvent attack or softening of the foam.

**Gypsum Dry Wall Adhesives.** Gypsum wallboard has been installed with adhesives since the 1950s. The use of adhesives results in a great reduction in the number of nails that are necessary, and at the same time virtually eliminates nail popping. Racking strengths are greatly enhanced if the gypsum wallboard is bonded to the stud walls. At the same time, there is less need for spackling and finishing the nail heads. The mastics used in this application will again bridge framing irregularities in the stud walls and result in more level and flat wall surfaces than nailing to bowed or warped studs. Today most good installations of gypsum wallboard are made with quality adhesives.

**Ceramic and Mosaic Wall Tile Adhesives.** These adhesives are generally emulsion systems with a long working time as well as a high degree of green grab that prevents the tile from sliding down a vertical surface. All ceramic tile cements today are troweled by notched trowel spreader, whose notch spacing is recommended by the adhesive manufacturer on the label.

**Wood Glues.** While wood glues are normally thought of in relationship to furniture and cabinet making, they have become important in construction also. Most finish carpenters utilize one of the various types of wood glues on trim around doors, windows, base board or other types of trim in the finishing process of construction, whether residential or industrial.

*White glues*, based on polyvinyl acetate, are of course quite common, but there is a trend toward the *aliphatic resin yellow wood glues* for this finish work. Not all yellow-colored glues are based on aliphatic resin. One advantage of the aliphatic resins is their built-in heat resistance, which allows them to be sanded where the white glues would gum up the sand paper. Also, they dry quite rapidly, faster than most white glues. The true aliphatic resin can be detected by the fact that it has a tacky characteristic normally not found in white glues.

*Liquid hide glues*, while still available, are

passing out of vogue in construction applications because of their slow drying characteristic. Generally speaking, white glues and aliphatic resin wood glues greatly outperform the liquid hide animal glues on construction applications.

## CEILING TILE APPLICATIONS

Several years ago, virtually all acoustical ceiling tile was installed with adhesives. Today, most installations are drop-in types with grid systems. There still are some instances however where the acoustical tile is still bonded to the ceiling, requiring a special kind of adhesive or mastic formulated from low molecular weight tackifying resins.

When adhesives are applied to the back of a 12" × 12" ceiling tile in golf ball size globs, there is a dead load placed on the adhesive bond from the weight of the tile. Generally, these ceiling tiles are tongue-and-grooved, and this accentuates the problem. Thus, the adhesive is required to have a high degree of cohesive strength to hold the tile in position and not allow it to sag away from the ceiling. This cohesive characteristic is not available in most adhesive formulations, except for the resin-based mastics. Consequently, most acoustical tile cements are formulated from resin base rather than rubber base. Mastics deficient in cohesive strength will fail.

## FLAT HORIZONTAL SURFACES

In today's construction, flat surfaces may involve plastic laminate, cultured marble, or acrylic countertop. Formerly, most of these products were installed on plywood. Today, however, various types of hardboard, particle board, or wafer board provide suitable substrates.

Contact adhesives are preferred for the plastic laminate materials. Contact cements are available in three types: water base, flammable solvent base, and chlorinated solvent non-flammable base. The vast majority of these contact cements utilize neoprenes as the basic elastomer. Attempts have been made by some manufacturers to formulate acrylic contact cements, but as of this writing none of these are in general use in the construction industry.

Water base contact cements will generally require greater pressures for ultimate bond strengths than can normally be accomplished on the job site. As a result, they are relegated to the cabinet shops and areas where controlled conditions and uniform pressures can be applied. They tend to be absorbed into the substrate, resulting in a "starved" glue joint. Thus, in the event a water base cement is used, adequate thickness of adhesive is essential. Many times this may require two or even three coats of the contact cement. Of course, both the plastic laminate and the substrate need to be coated.

Solvent base contact cements are among the most hazardous adhesives to use on the job site. Frequently, adequate ventilation is difficult to achieve and accumulation of vapors can result in fire and/or explosion. This characteristic became such a problem a few years ago that the federal government, through the CPSC (Consumer Products Safety Commission), banned contact cements with flash points below 20°F from the consumer markets. This ruling has resulted in broader acceptance of chlorinated solvent contact cements. The small increase in price is well worth the reduction in hazard from flammability and explosion. Chlorinated contact cements resemble flammable contact cements in both application and ultimate properties.

Cultured and/or acrylic based marble countertops are not necessarily installed over plywood or particleboards; some are bonded to framing members of countertop construction with high quality construction adhesive. While some of the SBR construction adhesive would work satisfactorily, the traditional mastics have been of the neoprene class. They are extruded from cartridges onto the cabinet framing, and bridge the framing irregularities that are generally present. Because of the translucency of cultured and acrylic marbles, it is generally desirable to select mastics that are light in color to avoid shadowing through the counter top.

## SPECIALTY ADHESIVES

A number of adhesives, glues, and cements with unique properties are used in the construction industry for special applications. The ros-

ter will undoubtedly grow in the future, and the list below is by no means all-encompassing.

### **Cyanoacrylate Adhesives**

Sometimes referred to as “super glues,” these remarkable adhesives provide extremely high strength and quick setting times. Cyanoacrylate adhesives, like their cousins the anaerobics, cure in the absence of oxygen. Thus, they are best suited for the bonding of nonporous surfaces such as plastics, glass, metal, plastic laminates, etc. Extreme caution should be used in their handling, because setup time is so rapid that smears of the adhesive on fingers can result in gluing fingers together.

### **Epoxy Adhesives**

These products are more generally used in manufacturing than in the construction industry and particularly on the job site. Generally two-part systems, they utilize curing agents that will impart their own particular characteristics to the cured formulation. Many types of curing agents are available for epoxies. Some of the amine curing agents can cause dermatitis, and cause violent reactions with evolution of heat. Usually, however, epoxy systems available over the counter utilize polyamide curing agents that are much easier and safer to handle. Thorough and complete mixing of the curing agent and epoxy is imperative to develop optimum properties. Thus the epoxies are difficult to use in job-site construction.

### **Resorcinols**

Resorcinol-phenol-formaldehyde is one of few totally waterproof adhesives available today. Again, this is a two-part system that has limited life after mixing the two components. The resorcinol adhesives cure at ambient temperature above 45°F; they can thus be used to build large wooden arches that must be totally waterproof.

### **Nitrile Rubber (Acrylonitrile-Butadiene Rubber) Adhesives**

These were developed in the 1930s as Buna-N adhesives, suitable for the fabrication of aircraft structures. They have had some use in

curtain wall construction. While they can be prepared in low viscosity, most of the products for the construction industry today would probably fall into the heavier mastic classification. They have uses similar to general construction adhesives, and are in fact often referred to as construction adhesives. Blended with phenolic resins, they are superior in heat resistance, oil resistance and strength to the lower-priced SBR construction adhesives.

### **Polysulfide Adhesives**

While polysulfides are better known as caulking materials, they are also strong, water-resistant adhesives with great flexibility. They are formulated as one-part systems that cure or set by reaction with moisture from the atmosphere. They have not been readily available. Sulfide odor is a problem, especially for the do-it-yourselfer.

### **Silicone Adhesives**

Silicone rubber is also used primarily as a caulking material. However, its tough rubbery consistency will lend it to various construction applications in the future and more silicone based adhesives will be sold over the counter.

### **Hot Melt Glues**

These glues, based on ethylene-vinyl acetate copolymer, polyamide, polyethylene and other resins, are generally applied from electric glue guns. They have rather sharp melting points that render them liquid at one temperature and solid when they cool a few degrees. They are excellent where quick bonds are desirable. However, they are best suited to spot applications rather than larger areas. One must work fast with these formulations because once they begin to cool, they set up very quickly, generally within a matter of seconds.

## **PROBLEMS AND TROUBLE SHOOTING**

Very few building products are totally infallible and completely trouble free. Adhesives are certainly not immune to problems. Unfortunately, when something has not been properly bonded, the adhesive is blamed where in fact in most cases some other factor has caused the

problem. Thus it is necessary to be cognizant of the potential sources of trouble. The conditions outlined below are but a few that seem to occur more frequently than others.

### **Freeze-Thaw Stability**

Latex or emulsion adhesives contain water, and may freeze. While many are called "freeze-thaw stable" by virtue of hydrophilic organic constituents, others can be harmed by freezing. The signal to the user is the notation on the label, "Keep from freezing." Fortunately, it is generally not possible to use a product that has been damaged by freezing. If it is not freeze-thaw stable, the adhesive may coagulate upon freezing and cannot be removed from the container. Adhesives that are freeze-thaw stable can generally go through a number of cycles of freezing and thawing without damage.

### **Improper Storage of Product**

Adhesives should be stored at room temperature for 24–48 hours prior to use during the colder winter months. Even those that are not harmed by freezing have a tendency to thicken when cold and are hard to use.

Some adhesives are packaged in fiber containers such as cartridges. These can be damaged and weakened if stored in a damp area, and the adhesive may lose solvent and become heavy or even hard. Sometimes this is undetectable until one tries to use the adhesive.

### **Incorrect Product for Application**

Adhesives partially utilized for one project may be quite unsuitable for another. Also, a leftover adhesive may be irretrievably changed in composition and physical characteristics.

### **Adverse Effects of Adhesive on the Adherend**

It is important that the materials being bonded and the adhesive or glue be compatible. The sensitivity of polystyrene foams to attack by certain solvents has been mentioned. Adhesives tend to bleed through some thin or porous surfaces. The solvents used in various adhesive formulations may harm the plastics and interfere with bonding. If there is doubt about the effect that an adhesive may have upon the ma-

terials being bonded, a trial should be made with scraps of the adherends. After 24 hours, the substrates should be pried apart and the bond and surfaces examined.

### **Materials Unreceptive to Bonding**

**Unclean Surface.** This is one of the most common causes of adhesive failure. Dust, dirt, loose scaly paint, oil, grease, etc. must be removed. Never clean with gasoline or fuel oils as they leave an oily residue. If you use solvents for cleaning, be careful to observe all recommended safety precautions.

Sometimes it is necessary to clean walls, ceilings or floors with a strong detergent or agent such as trisodium phosphate. All waxes must be removed from old existing floors before any attempt to adhere a new material. If there are any loose tiles or floor depressions of any type, they should be removed and the area of depression leveled with a latex concrete bonder or floor leveling compound.

### **Tolerances Too Great (Too Much Gap Filling).**

Another common cause of failure on adhesive installation is gaps or dips in the subfloor. Even smooth-troweled concrete that is clean and dry can sometimes cause problems through puddling. For example, if a concrete floor, even a new one, is hosed down with water, some puddles of water accumulate in the low areas. Should one be putting down a rigid flooring material such as slate, quarry tile, or wood parquet, it is possible that a gap would form between the flooring and the subfloor as the flooring would tend to bridge over the low points. In severe cases the adhesive that was troweled onto the subfloor may be prevented from coming into contact with the flooring, and an inadequate bond would be developed. These low places in floors as well as all cracks should be leveled and filled with a suitable latex-concrete underlayment before any attempt is made to install flooring. Mastic-type adhesives will perform some gap filling functions; but all too often too great a burden is placed on the mastic to fill too large a gap.

**Surfaces Not Dry.** One final problem which may cause interference with bonding is a moist surface. Most adhesives are not designed to

bond to wet surfaces. Damp masonry walls and concrete slabs are particularly troublesome. Even though a wall or floor may appear dry, surface water can seep through masonry walls during heavy rains and hydrostatic pressure can develop in floors. Adhesives and glues are not waterproofing compounds, and should not be used for this purpose even if they are called rubber based, waterproof, or water-resistant.

### **Improper Application of Adhesive or Glue**

**Incorrect Amount.** All too often an attempt is made to install wall or floor covering with an insufficient amount of adhesive. Even if the trowel notch size is correct, it may be partially clogged, or held at the wrong angle, or worn down from long use on concrete.

### **Adhesive Too Dry Before Assembly Made.**

Several factors may cause poor bonds as a result of excessively dried adhesive: the size of the bead from a cartridge; the size of the notches on the trowel; failure to wet the substrates; ambient temperature too high and humidity too low; and too long a waiting period before assembly.

1. *Trowel and cartridge application.* The open or working time of most adhesives is one of the variables that is generally controlled by the manufacturer through formulation. A bead extruded from a cartridge will generally have a shorter open or working time than a troweled material. The manufacturer will recommend on the label the exact bead size or notch trowel size for optimum results. Too small a bead or notch can greatly reduce the open or working time, thereby causing the adhesive to be too dry to develop a satisfactory bond.
2. *Nature of substrates.* Surfaces differ in porosity or absorbency. Particle board is made from different wood species, some more porous than others, so that solvents or water are absorbed more readily, thereby shortening the open or working times. Steel-troweled concrete is also far less porous or absorbent than regular masonry concrete, and as a result, solvents

are dissipated less rapidly. Metal or glass surfaces will not permit the drying or release of solvents as quickly as will wood or similar surfaces. In general the open or working time will not be nearly as long on porous materials as on nonporous materials.

3. *Temperature and humidity conditions.* Higher temperatures result in a more rapid release of the solvents, thereby shortening the open or working times. However, humidity also plays an important role. Even if the temperatures are high, solvent release under high humidity conditions could be extremely slow, resulting in a much longer open or working time. Of course, the presence of air flow or wind would also tend to shorten open times.
4. *Waiting period too long.* While any one or a combination of the above factors could create problems, probably none are as common as just plain waiting too long after the adhesive is applied to make the assembly. On any job it is wise to occasionally pull apart an assembly shortly after it is made just to make sure that there is wet adhesive transfer from one surface to another.

**Adherends Improperly Positioned, Clamped, or Braced During Drying.** Positioning is very important. In the case of contact cements there is no second chance to position the substrates, since bond is instantaneous. In other types of installations the correction of improper positioning can result in too much adjustment, thereby wiping adhesive from one of the substrates, resulting in a starved joint, a bond with inadequate adhesive.

Improper clamping or bracing can also create problems. Not having the assembly in close enough contact during drying or curing will result in an unsatisfactory bond.

### **Bonded Assembly Improperly Set, Cured, or Dried**

Many good bonds are destroyed by moving the assembly about before the adhesive or glue has had an opportunity to adequately cure, dry, or set. There is wide variation in the curing or



drying characteristics of different kinds of glues and adhesives. Some good wood glues cure in a matter of minutes, while a so-called fast-drying rubber mastic might take 12–24 hours to develop a satisfactory bond. The directions on the label or manufacturer's instruction sheet must be followed.

### **Adhesive or Glue Did Not Meet Performance Requirements of Bonded Assembly**

Where and how is the final bonded assembly going to be used? This is a key question that is sometimes overlooked. All too often the final assembly will stand outdoors in all kinds of weather, yet a waterproof adhesive has not been selected. Many manufacturers are inclined to take some poetic license in describing their products as “water resistant” or “waterproof.” If the product is to be used outdoors, the label should not only state “waterproof” but also describe the conditions under which the adhesive can be used and will perform. Most wood glues are not waterproof and should not be exposed to exterior conditions.

Temperature is another consideration. Many adhesives are exposed to temperatures, partic-

ularly in roof and ceiling applications, that they were never designed to tolerate. Some adhesives have poor metal adhesion yet bond well to wood and other surfaces. Strengths are also to be considered. It makes no sense, for example, to use an epoxy adhesive that will develop thousands of pounds per square inch of strength when even one of the substrates will fracture with only a few hundred psi or less of shear stress.

### **Have Not Read the Manufacturer's Instructions**

A thorough reading of the manufacturer's label and directions would go a long way towards preventing some of the trouble areas that are occasionally encountered. After all, the cost of the adhesive or glue is only a minute part of the total cost in terms of time, labor and materials.

## **BIBLIOGRAPHY**

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# Adhesives in the Electrical Industry

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The use of adhesives in the electrical industry is rapidly expanding because adhesives are being developed having characteristics suited to the unique needs of electrical/electronic market. Also the electrical industry has gained faith in the reliability of adhesives.

Some of the major recent developments in the adhesives used in the electrical industry are: the emergence of specially tailored surface mount adhesives; the increased use and proliferation of polyimides; the purification of die attach adhesives and other materials coming in close contact with IC dies; and the use of high molecular weight epoxies in sealing flat panel displays.

Adhesives are used in the electrical/electronic field in a variety of ways, from holding microcircuits in place to bonding coils in mammoth electrical generators. Failure of adhesives could cause computers to stop functioning, cities to black out, or missiles to misfire.

In addition to mechanically fastening, adhesives in electrical applications are required to conduct heat, conduct or isolate electricity, provide shock mounting, seal, and protect substrates. Properties required for various applications cover the range from life of a few seconds to many years. Operating temperatures are from  $-270^{\circ}\text{C}$  to  $500^{\circ}\text{C}$ . Adhesives are used in quantities of less than a microgram to more than a ton. The adhesive choice is governed by these considerations plus strength,

thermal conductivity, application methods, cure temperature, and environmental exposure.

Epoxies are the most widely used adhesives because of their versatility, excellent adhesion, compatibility, ease of application, good electrical properties, and resistance to weathering. Silicones are used where flexibility, wide temperature range, high frequency, high humidity, and/or atmospheric contamination are encountered. Hot melts can be used where their lower strength and limited temperature range can be tolerated and rapid assembly is important. Acrylics are used because of their excellent electrical properties, stability, good aging characteristics, optical clarity, and rapid curing. Urethane adhesives have flexibility, toughness, and strength from cryogenic temperatures to  $125^{\circ}\text{C}$ . Precoated polyvinyl butyral produces bonds which are tough and are easily fabricated. Ceramics and glasses of many compositions form high temperature and hermetic seals. Adhesives are available as one-part liquids, two-part liquids, powders, solvent solutions, films, thermoplastic rods, and preformed pellets.

## MICROELECTRONICS

### Die Bonding

Three major uses of adhesives in microelectronics are die bonding, bonding circuit elements to substrates, and sealing electronic

packages. The processing temperature of the adhesive is much lower than the temperatures required by eutectic bonding, which degraded chip properties. In die bonding, a microdrop of adhesive as small as 0.003" in diameter is dispensed onto the substrate in a precise location. The integrated circuit chip is placed accurately into the adhesive, which is then heat cured. The amount and location of the dispensed adhesive are critical; too much will result in a bond line which is excessively thick. The viscosity and surface tension must be high enough to hold the chip in place and the adhesive must not thin out to the point where it will flow and insulate circuit pads. Thinning (reduction in viscosity) would allow filler settling and the chip swimming out of its proper location. One- and two-part specially formulated epoxies and polyimide adhesives are used for die attachment.

Polyimides became popular as die bonding adhesives a few years ago because the then available epoxies contained ionic contamination that caused failures. Polyimides are inherently "cleaner" than epoxies because of their method of manufacture. Polyimides are stable at much higher temperatures than epoxies but they always are applied out of solvent solution and require much higher cure temperatures. The epoxy formulations now in use generally con-

tain less than 50 ppm ionic impurities. Table 1 lists the epoxy components and their affect on the properties of the cured adhesives. Table 2 gives properties of a typical die attach adhesive. The adhesives must be capable of withstanding subsequent fabrication stress, such as the 400°C encountered in thermal compression lead bonding.

Some chips are very sensitive to gaseous atmospheric contamination. Solvents and some curing agents, e.g., amines and fluorides have been reported to affect CMOS and other ICs. All organic adhesives release water vapor in hermetically sealed packages. The level of water vapor must be kept below 15,000 ppm to avoid chip deterioration. Adhesives are available that contain getters to bind the water and thus eliminate this problem. As other chemicals are also released from the adhesives on aging, and different chips have varying degrees of sensitivity to contaminants, each circuit must be checked with the chosen adhesion formulation.

Besides holding the chip in place, the die bonding adhesives generally must conduct heat from the chip to the heat sink. This requires a high thermal conductivity and minimum of voids in the bond line. Electrically conductive adhesives are used where the back of the chip

**Table 1. Constituents of Epoxy IC Adhesives.**

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<i>Base Resin</i>	
1. Bisphenol A—epichlorohydrin resin (bis A), most widely used, liquid at room temperature	
2. Novolak epoxies—good for high temperatures, brittle, semisolid, or solid at room temperature	
3. Solid bis A resin—for preforms and films	
<i>Curing Agents</i>	
1. Dicyandiamides plus accelerators—one-part systems, long shelf life, 150°C cure	
2. Acid anhydrides plus accelerators	
3. Aromatic substituted ureas	
<i>Fillers</i>	
Aluminum oxide, boron nitride, magnesium oxide, and silica; particle size, 1–2 microns	
<i>Reactive Diluents</i>	
(lower viscosity of mix)	
Butyl glycidyl ether, phenyl glycidyl ether	
<i>Solvents</i>	
1. Butyl cellulosolve—for screening	
2. Xylene and MEK—for spraying	

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**Table 2. Typical Epoxy Die-Attach Adhesive Properties.**

Storage Life:	One-component system—6 months
Curing Cycle:	One-component—1 hour at 125°C, 30 minutes at 150°C, or 24 seconds at 270°C
	Two component—15 minutes at 120°C
Resistivity:	10 <sup>12</sup> ohm-cm at 150°C
Tensile Strength:	To gold surface—1,000 psi
Outgassing:	24 hours at 125°C under 10 <sup>-6</sup> Torr. Maximum weight loss—1% Maximum condensibles—0.1%
Temperature:	Exposure without permanent loss of properties: 400°C for 5 minutes 150°C for 1,000 hours
Repairability:	Adhesive bond sufficiently weakened at 200°C to 250°C to permit nondestructive chip removal
Specifications:	Curing agents prohibited—primary and secondary amines Chemicals prohibited—those that release excessive water and/or ammonia Ionic contamination—less than 50 ppm of chlorine, sodium, and potassium

contains a circuit connection, e.g., grounding. (Electrically conductive adhesives are covered in another section of this book.)

### Component Attachment

The next level of microelectronic adhesive bonding is adhering the IC packaged chip, capacitors, and resistors to hybrid circuits. Epoxies with properties similar to die bonding adhesives are used. In multichip applications the adhesive is often screened onto the ceramic substrate. Film adhesives with and without glass cloth carriers are also used. The film is solid, semi-cured epoxy which is cut to the chip package size. On heating, the epoxy melts and then sets during the curing cycle.

Solvents used in the manufacture of the films are not always completely removed. During the cure cycle, solvents can form gas pockets producing inferior, porous bonds. In some circuits the solvents can affect the electrical characteristics of the component.

### Package Sealing

Film adhesives are also used to seal integrated circuit packages. The film, cut in the form of a frame, is positioned on the bonding ledge, the lid is put in place and the unit is heated to melt the adhesive and cure it. This process assures the correct amount of adhesive in the proper place and minimizes adhesive runoff.

Ceramic frits and metal solders are also used to seal IC packages when hermetic seals are required. The ceramic is applied to the substrates out of a suspension. The solvent is evaporated and the binder burned out. The cover is then put in place and the glass frit is melted to produce the bond. Properties of the ceramic and glass are given in Table 3.

### PRINTED WIRING BOARDS

The necessity to resist 250°C soldering temperature limits the adhesives that can be used to bond copper foil to laminated printed wiring boards. The copper foil can be bonded during the lamination operation if the base resin has sufficient adhesive strength. If the foil is applied to the cured board it is first coated with a B-staged epoxy or thermoplastic and then heat bonded. A film of B-staged epoxy or polyvinyl butyral can be used in place of the precoat.

Copper foil is adhered to polyester film based flexible circuitry with a thermoplastic polyester adhesive. This produces a bond having lower operating temperature than the other adhesives cited. When polyimide film such as DuPont's Kapton is used as the high temperature flexible circuit substrate, a thermoplastic FEP Teflon coating or epoxy, acrylic, or polyimide adhesive is used to bond the foil.

When printed circuit assemblies are subjected to shock or vibration, components must be held in place with circuit board coatings or

**Table 3. Glass/Ceramic Sealing.**

<i>Types</i>
<ol style="list-style-type: none"> <li>1. Stable glass—melts and solidifies without phase change, like thermoplastic plastics, most contain about 70% lead</li> <li>2. Devitrifying glass—melts and crystallized to a high temperature ceramic, has low coefficient of thermal expansion, not transparent, low temperature processing—430 to 500 C.</li> </ol>
<i>Uses</i>
<p>In cathode ray tubes, IC packages, liquid crystal displays, and gaseous discharge tubes</p> <p>Die attach</p>
<i>How Applied</i>
<ol style="list-style-type: none"> <li>1. From a slurry: (a) glass powder suspended in amyl acetate or butyl carbitol with nitro-cellulose or ethyl cellulose binder; (b) slurry is screened onto substrates or deposited by other methods; (c) solvent evaporated below 200°C, (d) binder burned off at 150–300°C; (e) glass is fused at 450°C for one hour</li> <li>2. Perform—dry and ready for fusion</li> </ol>

adhesives. Highly filled epoxies cured at low temperature with amines are often used. Thermal cycling can crack bonds if the thermal coefficient of expansion of the adhesive differs greatly from that of adjacent objects. It may be necessary to cushion glass components with a soft silicone rubber interface before bonding to prevent their cracking.

## LARGE EQUIPMENT

The physical and electrical requirements for generators, transformers, and other large equipment are becoming increasingly stringent. They must operate at elevated temperatures for 20 to 40 years in hostile environments. Current surges which displace coils and high rotational speed put physical stress on the equipment. The size of many pieces of equipment preclude the possibility of curing in ovens and the heat conduction of copper and other metal makes local heating impractical. Room temperature setting adhesives overcome these difficulties.

Often components such as coils are bonded and insulated before assembly. High voltage insulation around coils is formed from fabric impregnated with epoxy, polyester, or silicone varnishes. Glass or polyester cloth is wound into the coils. The cloth acts as a spacer which is subsequently impregnated by the resin. The resulting reinforced fabric bonds the coil into a strong monolithic structure with high dielectric

strength. Phenyl modified silicones are used as impregnant up to 220°C. They offer excellent penetration into the interwinding fabric and moisture protection. For 185°C operation, polyesters based on isophthalic acid or terephthalic acid or RTV silicones are used. Where high voltage insulation up to 155°C is required, epoxies cured with anhydrides of dibasic acids are the impregnants of choice.

B-staged epoxies and polyesters in glass cloth are used to bind and tie armatures, transformers and coils together. This reinforced material replaces previously used steel bonding, which had to be carefully insulated to eliminate shorting other electrical components. Acrylic resins on glass cloth or Nomex is used in hermetic and general purpose motors because of their resistance to DuPont's Freons, solvents, and oils.

## Pressure Sensitive Adhesives

Pressure sensitive adhesive tapes are used for holding and anchoring lead wires to the outer wrap of transformer coils, capacitor wrapping, protection of leads and coils, and other similar applications. Adhesive transfer films are used to hold insulating material in position. Natural rubber based pressure sensitive adhesives have poor solvent resistance unless they are cross-linked. Many modifications are possible. Synthetic rubber has better stability than natural rubber and better solvent and ozone resistance. Acrylic pressure sensitive adhesives have the best balance of properties. They maintain their

excellent electrical properties and solvent resistance after aging at high temperature and can be crosslinked if desired. Silicones are only pressure sensitive adhesives suitable for 180°C operation. Also, they can be applied at lower temperature than the others. Adhesive tape backing include films of polyester, polyethylene, polyvinyl chloride, polyimide, polytetrafluorethylene and others.

It is important to check the compatibility of the pressure sensitive adhesive with the magnet wire used to be sure that there is no deterioration of the wire enamel and reduction of dielectric strength. High sulphur and chlorides will adversely affect the copper wire especially in the presence of humidity and pollution.

### Bonded Mica

Shellac or alkyd resin is used to bind mica splittings to produce mica board. This is pressed into shapes used as insulation in electric motors, generators, and transformers. Mica tape is used as insulation in motors and generator coil slots. Mica tape is fabricated by bonding mica flakes to glass cloth or tissue paper with shellac or silicone resin.

### Displays

Bonding and sealing liquid crystal displays must be done in a carefully controlled way with carefully selected materials to assure moisture exclusion and no deterioration of the liquid crystal component. Thermoplastic, high molecular weight epoxy resins without catalyst are widely used as the sealing medium. Some manufacturers use a 0.0005" thick polyester film spacer coated with B-staged epoxy. Glass seals, described in Table 3, are used in liquid crystal displays and gaseous discharge displays.

## SURFACE MOUNTING ADHESIVES

On printed wiring boards containing surface mounted and through-hole attachments, it is necessary to secure the chip components to the bottom of the board before soldering. A number of specialized adhesives have been developed to do the job. These adhesives hold the components in their correct positions through board handling, cleaning, flux application, and soldering, and must not weaken or change shape during these exposures.

The adhesive has minimal function after the soldering application, but it must not reduce the reliability of the circuit by becoming conductive during environmental exposure, or put stress on the components during thermal cycling or mechanical handling. On the other hand, if component replacement is necessary, the adhesive should soften sufficiently at soldering iron temperature to allow part removal.

Many of the currently available adhesives have the required cured properties for use in component staking, but do not have the necessary application properties. High speed adhesive dispensing equipment requires adhesives with extended pot life and smooth flow characteristics. The formed adhesive mounds must retain their shapes without slumping and must have enough green strength to hold the components in place through the curing cycle. The adhesive must not string or tail as the dispensing tip is withdrawn. The resin component must not migrate onto contact pads where it would cure and interfere with soldering. The adhesive should cure rapidly with heat and/or UV exposure.

Several types of adhesives have been formulated to have the properties required to attach surface mounted components. Some of the typical products are listed in Table 4 with their

**Table 4. Typical Surface Mount Adhesive.**

	<i>One-Part Epoxy</i>	<i>One-Part Frozen Epoxy</i>	<i>UV-Curing Methacrylate<sup>a</sup></i>
Storage life at room temp.	3 months	4 hours	6 months
Cure time: 150°C	3 min	5 sec	40 sec
120°C	10 min	10 sec	2 min

<sup>a</sup>Can be cured with UV lamp alone if light can reach entire body of adhesive. Exposed adhesive can be partially cured in 10–30 seconds with UV and the completely cured with heat.

properties. These adhesives can be applied by silk screening, dispensing from a single tube or multiple tubes, or pin transfer.

## FORMS OF ADHESIVES AVAILABLE

### Two-Part Systems

**Examples.** Epoxy, polyurethane and silicone.

**Advantages.** Very long shelf life, very fast cure and room setting possible, properties can be varied by using different curing systems.

**Disadvantages.** Short pot life, excess mixed material is wasted, possibility of improperly proportioned or mixed adhesive producing inferior results.

**Applications.** General use, cementing components to printed circuits.

### One-Part Liquids—Heat Curing

**Examples.** Epoxy and polyimide.

**Advantages.** No mixing, no pot life problems, and no waste.

**Disadvantages.** Necessity for high temperature cure, shelf life and storage conditions are critical.

**Applications.** IC chip bonding and impregnation.

### One-Part Liquids—Moisture Curing

**Examples.** RTV silicones and polysulfide rubber.

**Advantages.** Excellent adhesion to a variety of substrates including silicones, room temperature setting, and ease of use.

**Disadvantages.** Acetic acid given off by some silicones, need of permeable adherend.

**Applications.** Cementing silicone gaskets in place, sealing wire harnesses.

### Films—Supported or Unsupported

**Examples.** B-staged epoxy, rubber phenolic and polyvinyl butyral.

**Advantages.** Precise amount and shape applied to correct location, accurate spacing of adherents and control of spreading.

**Disadvantages.** Expensive, mating surfaces must be parallel, heat and pressure required.

**Applications.** Sealing IC packages, cementing copper foil to printed wiring boards.

### Preforms—Solid Shapes That Melt to Viscous Liquid and Cure with Heat

**Example.** B-staged epoxy cylinders.

**Advantages.** Accurate amount of adhesive put in optimum position, controlled flow, no waste, high speed production.

**Disadvantages.** Expensive, carefully controlled heat cycle required.

**Applications.** Sealing caps on vacuum tubes and sealing switch terminals.

### Thermoplastic

**Example.** Ethylene vinylacetate based hot melts.

**Advantages.** Very rapid application and setting, no waste and inexpensive.

**Disadvantages.** Heated application equipment necessary, bonds have moderate strength, not useful at high temperature.

**Applications.** Tacking wire in place, bonding voice coil to speaker cone.

### Pressure Sensitive Adhesive

**Examples.** Rubber or acrylic PSA on polyester tape.

**Advantages.** Instant adhesion at room temperature, substrate supplied with adhesive, easily removed.

**Disadvantages.** Limited temperature, low strength, creep.

**Applications.** Securing transformer coil in place, positioning lead wire to coil.

### **Solvent Systems**

**Examples.** Rubber, rubber phenolic, acrylic.

**Advantages.** Rapid application, inexpensive, wide range of bonding methods and substrates.

**Disadvantages.** Solvent removal necessary, high cure shrinkage.

**Applications.** Labels and insulation lamination.



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# Conductive Adhesives

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Polymeric materials are normally excellent insulators. Most of the resins, such as epoxies, that are used in today's best adhesives are prized for their ability to insulate metals and other surfaces from both heat and high electrical voltages. But for many important industrial applications, particularly in the electronics industry, it is necessary that an adhesive be able to *conduct* either heat or electricity, or both. Conductive adhesives, therefore, owe their conductivity as well as their cost and most other physical properties to the incorporation of high loadings of metal powders or other special fillers of the types shown in Table 1.

## ELECTRICAL CONDUCTIVITY

Table 1 shows the electrical conductivity values and densities for pure silver, copper, gold and other metals; for the best current electrically conductive adhesives and coatings; and for oxide-filled and unfilled insulation resins. Although a large number of metals might be considered, in powdered form, to make conductive adhesives, most high performance conductive products today are based on flake or powdered *silver*. Silver has the disadvantage of being relatively expensive, currently selling for

between \$5 and \$8 per troy oz.\* vs. about 30¢/oz. for powdered copper. The price of silver has stabilized during the past nine years, and silver continues to offer advantages in conductivity *stability* which cannot be matched by copper or other lower cost metal powders.

Figure 1 shows the mechanism for current flow through a metal-filled polymer. If enough metal particles are added to form a network within the polymer matrix, electrons can flow across the particle contact points, making the mixture electronically conductive. Even under the most favorable circumstances, current flow occurs only over the small area of the contact points, so the conductivity of even the best current silver-filled products is two orders of magnitude lower than the conductivity through pure silver.

Figure 1 also shows the resistances which are introduced at the particle contact points by surface oxide layers, or by layers of absorbed organic molecules. It is this surface oxide layer that rules out the use of most metals in conductive plastics. Aluminum powder is widely used

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\*Prices for silver, gold, and platinum are normally quoted in newspapers and elsewhere in dollars/troy oz. One pound equals 14.5 troy oz. One troy oz. equals 31.1 grams.

**Table 1. Electrical Conductivity of Metals, Conductive Plastics and Various Insulation Materials at 25°C.**

<i>Material</i>	<i>Specific Gravity g/cm<sup>3</sup></i>	<i><math>\rho</math> = Volume Resistivity ohm cm</i>
Silver	10.5	$1.6 \times 10^{-6}$
Copper	8.9	$1.8 \times 10^{-6}$
Gold	19.3	$2.3 \times 10^{-6}$
Aluminum	2.7	$2.9 \times 10^{-6}$
Nickel	8.9	$10 \times 10^{-6}$
Platinum	21.5	$21.5 \times 10^{-6}$
Eutectic solders	—	$20-30 \times 10^{-6}$
Conductive glass adhesive	—	$1 \times 10^{-5}$
Best silver-filled epoxy adhesives	—	$1 \times 10^{-4}$
Graphite	—	$1.3 \times 10^{-3}$
Nickel-filled epoxy adhesives	—	$1 \times 10^{-2}$
Graphite or carbon-filled coatings	—	$10^2-10^1$
Oxide-filled epoxy adhesives	1.5-2.5	$10^{14}-10^{15}$
Unfilled epoxy adhesives	1.1	$10^{14}-10^{15}$
Mica, polystyrene, and other best dielectrics	—	$10^{16}$

in the adhesives industry as a reinforcing filler and as a decorative pigment, but aluminum powder cannot be used to make electrically conductive plastics because of the oxide film which insulates the particle contact points. Only metals such as silver and gold, which form both thin and relatively conductive oxides, can be used in powdered form to provide stable resistivity values less than about 0.001 ohm/cm.

#### Gold-Filled Adhesives and Silver Migration

Gold filler is sometimes specified for electronic assembly operations, despite the much higher price and lower electrical conductivity compared to silver-filled adhesives. Gold-filled adhesives are still required by some military specifications issued in the early 1960s.

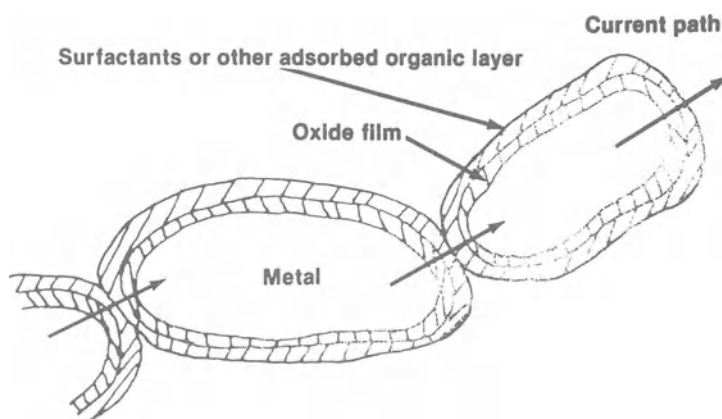


Fig. 1. Current flow path between metal particles in conductive adhesives. Adsorbed organic molecules and oxide films prevent or impede passage of electrons across particle contact points.

The justification for gold is that it avoids an effect called *silver migration* which occurs with silver-filled acrylics, epoxies, and other resins. Silver migration is dependent on the fact that all polymeric materials are permeable to water to some extent. In the presence of moisture, silver ions may be leached out of the cured resin, and redeposited elsewhere in the circuit.

To test for silver migration, a constant DC voltage is applied between a silver-filled adhesive and a nearby conductor, such that the adhesive is the anode, and the voltage gradient between the conductors is on the order of 1 volt/mil. Moisture vapor condensed on the intervening surface can permit silver ions to migrate toward the cathode and form a conductive path of metallic silver which short-circuits the device. Migration has traditionally been more of a problem in hybrid than in monolithic ICs, because the adhesive fillet may approach other conductors on the hybrid substrate.

There is no significant difference in silver migration for epoxies as compared to other thermosetting resins or to conductive glass adhesives. Silver ions can be extracted from all glasses and polymers with almost equal ease. Increasing  $T_g$  (glass transition temperature) of the adhesive has a slight, but not important, effect on reducing migration. Whether or not an adhesive is "clean" (low  $\text{Cl}^-$ ,  $\text{Na}^+$ , and other extractable ions) also has no significant effect on preventing silver migration. Previously it had been speculated that it was necessary to have ions present in the water film on the surface to "connect the cell" and initiate silver ion transport.

A lower cost alternative to gold-filled inks or adhesives is to substitute a silver-palladium alloy for the pure silver filler used as the conductor. When the alloy content of Pd exceeds about 30%, migration is retarded long enough to comply with Mil. Std. 883B, with no significant loss in conductivity, and with relatively small increase in cost relative to pure silver filler. Nickel-powder-filled adhesives offer another way to avoid migration, although at considerable sacrifice in electrical conductivity relative to gold or silver.

The best chemical method is to use a poly-

mer coating or potting compound over the silver-based ink or adhesive, to eliminate any direct diffusion path for ion migration. In the electronic industry, silicone gels and coatings are most often used for this purpose because of their ionic purity and their flexibility over a broad temperature range.

### Low-Cost Conductive Adhesives

In efforts to avoid the use of pure silver to provide conductivity, a number of lower cost conductive adhesives have appeared on the market during the past 20 years. Some of these products are based on nickel or carbon powders, others on copper that has been precleaned by an acid wash, to remove some of the surface oxides, or which has been plated with a thin surface coating of silver. For RFI shielding and other low-cost applications that do not require high electrical conductivity or exposure to elevated temperatures, some of these copper or nickel-filled adhesives have proven adequate. But copper-filled resins may not retain stable electrical conductivity at elevated temperature due to continued growth of oxide on the particle surfaces. A copper-filled epoxy will typically increase in resistivity by a factor of 100 after 48 hours in air at 150°C. Silver-coated glass beads, although more stable than silver-coated copper, have both rheological and conductivity limitations.

Much of the technology involved in conductive plastics involves the metal particle size and shape. Silver is normally used in the form of very small flakes. To minimize cost (i.e., silver loading), anisometric particles, such as rods or flakes, are used to give a higher number of contact points and higher conductivity than would spheres or cubic particles. But these flakes tend to orient parallel to the adherend surfaces during many bonding and coating processes. For bonding applications where electrical conductivity perpendicular to the bond line is required, this orientation can reduce conductivity and be a disadvantage.

Voids due to air bubbles or to solvent bubbles are a frequent quality problem in the bond line. These voids are undesirable because they

increase electrical and thermal resistivity and can also decrease bond strength. For this reason, the modern trend is to specify single-component, solvent-free, silver-filled adhesives, which are premixed and pre-degassed by the adhesive manufacturer before shipment to the customer and which contain no air bubbles, solvents, or other volatiles which can cause voids.

### Comparison of Conductive Adhesives to Solder

Increasingly, silver-filled adhesives are being used to replace tin, lead, and silver-based solders. A number of reasons account for this increase in use of conductive adhesives:

1. Electrically conductive adhesives give stronger and tougher bonds than most solders. Aluminum powder, which is used as the filler in many high performance epoxy adhesives, normally gives very high bond strengths as measured by ASTM-1002. Silver-filled adhesives, although generally considerably lower in strength than the best aluminum-filled structural adhesives, are nevertheless still much stronger and tougher than most soldered joints.
2. Epoxy adhesives wet and bond to almost all surfaces and can be used with virtually any combination of metals, glass, ceramic, or plastic. Conventional solders only wet certain metals. Other surfaces, such as silicon or alumina or tantalum oxide, cannot be soldered without gold plating or other costly surface modifications.
3. Conductive adhesives cure at much lower temperatures than are required for solder flow and permit use in contact with heat-sensitive components. Two-component conductive epoxies cure at room temperature.
4. Conductive adhesives eliminate the need for solder flux and for flux removal after bonding.

### THERMAL CONDUCTIVITY

Metal-powder-filled adhesives conduct both heat and electricity. Some adhesives, however,

must conduct heat but *not* electricity in order to bond power devices and other heat-generating components to heat sinks, and to other metal surfaces, where the adhesive must permit high transfer of heat plus electrical isolation. Heat-conductive coatings include spray-applied coatings for corrosion protection as well as high-voltage insulation.

Table 2 lists thermal conductivity values for several metals as well as for beryllium oxide, aluminum oxide, and several filled and unfilled resins. Fig. 2 shows the thermal conductivity for an epoxy resin as a function of volume fraction of heat-conductive filler.

Beryllium oxide is the most heat conductive dielectric material and is frequently used in sintered form as a heat sink, but it is generally not used to make heat-conductive adhesives because of the toxicity and high cost of powdered beryllia.

Alumina is inexpensive, provides excellent strength, and can be added to epoxy and silicone resins in very high concentrations before the viscosity becomes excessive. It is, how-

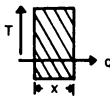
**Table 2. Thermal Conductivity of Metals, Oxides, and Conductive Adhesives.**

Thermal Conductivity at 25°C (Btu/hr°F ft/ft)	
Silver	240
Copper	220
Beryllium oxide	130
Aluminum	110
Steel	40
Eutectic solders	20-30
Aluminum oxide	20
Best silver-filled epoxy adhesives	1 to 4
Aluminum-filled (50%) epoxy	1 to 2
Epoxy filled with 75% by wt. Al <sub>2</sub> O <sub>3</sub>	0.8 to 1
Epoxy filled with 50% by wt. Al <sub>2</sub> O <sub>3</sub>	0.3 to 0.4
Epoxy filled with 25% by wt. Al <sub>2</sub> O <sub>3</sub>	0.2 to 0.3
Unfilled epoxies	0.1 to 0.15
Foamed plastics	0.01 to 0.03
Air	0.015

**Table for Conversion of Thermal Conductivity Units**

g cal/cm <sup>2</sup> sec °C/cm	w/cm <sup>2</sup> °C/cm	Btu/ft <sup>2</sup> hr°F/ft	Btu/ft <sup>2</sup> hr°F/in
1.0	4.19	242	2900
0.23	1.0	58	690
4.13 x 10 <sup>-3</sup>	0.0173	1.0	12.0
3.44 x 10 <sup>-4</sup>	1.44 x 10 <sup>-3</sup>	0.083	1.0

Heat transfer formula:  $q = \frac{k \Delta T}{x}$



$k$  = thermal conductivity  
 $\Delta T$  = temperature drop across material  
 $q$  = heat flow/unit area  
 $x$  = material thickness

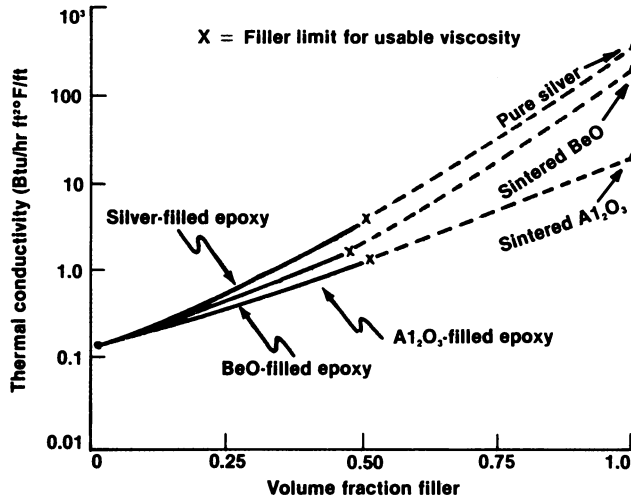


Fig. 2. Thermal conductivity increases as filler loading increases, but loading is limited by mixture viscosity to a maximum of 40–50% by volume.

ever, abrasive and may cause wear and other damage to dispensing equipment. Alumina-filled high  $k$  adhesives are processed to remove grits or other large particles that can prevent the attainment of very thin bond lines. Minimum bond thickness is almost always desirable because heat flow is proportional to the ratio of thermal conductivity to bond thickness.

The best current 100% solids epoxy adhesives contain about 70% aluminum oxide by weight and give thermal conductivities in the range of 0.8–1 in the English units shown in Table 2. For convenience, a conversion chart is included in Table 2 to permit conversion to any other set of units. The  $k$  values for the best alumina-filled epoxies are 10–12 times greater than for unfilled epoxy resins, but are still much lower than for pure metals or solders. Nevertheless, heat flow is adequate for bonding most components. For example, an adhesive with a thermal conductivity of 0.91 and a bond thickness of 3 mils would be able to transfer about 20 W/cm<sup>2</sup> of surface area, with a  $\Delta T$  only about 10°C above the heat sink temperatures:

$$\begin{aligned} k &= 0.91 \text{ Btu/hr ft}^2 \text{ }^\circ\text{F/ft} \\ &= 0.91 \times 0.0173 \\ &= 0.016 \text{ W/cm}^2 \text{ }^\circ\text{C/cm (Table 2)} \end{aligned}$$

$$\text{If } q = \text{power/area} = 20 \text{ W/cm}^2$$

$$\text{and } x = 3 \text{ mils} = 0.0075 \text{ cm}$$

$$\begin{aligned} \Delta T &= \frac{qx}{k} = \frac{20 \times 0.0075}{0.016} = 9.4^\circ\text{C} \\ &= \Delta T \text{ across interface} \end{aligned}$$

An unfilled epoxy adhesive, with a conductivity of about 0.1 in the same units would cause a  $\Delta T$ , for the same device, bond thickness, and power level, of almost 100°C.

Frequently, a permanent adhesive is undesirable, because some components must be capable of easy and repeated removal from heat sinks or other mounting locations. Mechanical fastening methods, such as screws, leave an undesirable air gap between the component and the heat sink, and cause heat buildup. Highly filled silicone compounds, frequently referred to as *thermal greases*, are used to eliminate this air gap. Special thermoplastic silicone resins are used which do not harden or crosslink. Hence, the device can be removed and replaced for maintenance purposes. The thermal grease must not decompose, give off volatiles, or permit any silicone bleed even after long-term exposure to high temperatures. The filler, normally zinc oxide, must have a maximum particle size under 1 mil to permit a tight fit. The best current thermal greases meet these requirements and provide the thermal conductivity of about 0.9 as in the above example.

## DIE ATTACH ADHESIVES

Silver-filled epoxy and polyimide die attach adhesives are used worldwide to bond dies to the substrates of hybrid and monolithic integrated circuits (ICs), light emitting diodes (LEDs), and other devices. A conductive adhesive permits large cost savings over previous die attach methods involving gold-silicon eutectic solder. The adhesives bond to bare silicon, to gold, to copper, to alumina, and to other surfaces without requiring the prior gold metallization needed for eutectic bonding, and without requiring any scrubbing or bake-out.

Solder bonding requires process temperatures over 300°C. Adhesives, however, cure at much lower temperatures and provide yield improvement with LEDs and other heat sensitive devices. Moreover, epoxies have more useful flexibility than solder or glass and are, therefore, less likely to cause cracking of large dies during cool down. Fig. 3 shows the most widely used method for packaging integrated circuits. The low cost plastic (epoxy) packages called P-DIPs (plastic dual inline packages) are used in high volume consumer products, such as games, calculators, watches, TV, radio, and audio equipment.

### Die Bond Adhesive Performance Requirements

The properties needed for a successful die bond adhesive depend on the nature of the final IC or other device, but generally can be divided into performance requirements needed for high speed, high yield production, and reliability requirements needed to insure that the adhesive

can cause no loss in function or reduction in expected life time of the finished device.

### Viscosity and Flow Properties

Die attach adhesives are creamy, thixotropic pastes which must be dispensed rapidly and without dryout, stringing, or other flow problems, to permit high yields and high production rates. Most ICs are made by dispensing a very small, but carefully shaped, droplet of adhesive on the lead frame or other substrate, using automatic die bonding equipment. The adhesive must have enough green strength to prevent chip movement before cure, must form a proper fillet height and shape, and must not permit any resin bleed before or during cure.

### Hot Strength and Thermal Stability

Die bond adhesives must generally develop high hot strength after a short cure period in order to resist displacement of the die during subsequent wire bonding. Adhesive temperatures may reach 300°C during some wire bonding operations. Modern epoxies and polyimides retain sufficient strength to resist transverse forces during wire bonding.

### High Purity Adhesives For Other Electronic Assembly Operations

Conductive adhesives are used for many other electronic assembly operations, in addition to die attach. Epoxy paste adhesives are used for capacitor and other component attach in hybrid components or on printed circuit boards. In general, these electronic assemblies require high purity adhesives which do not give off im-

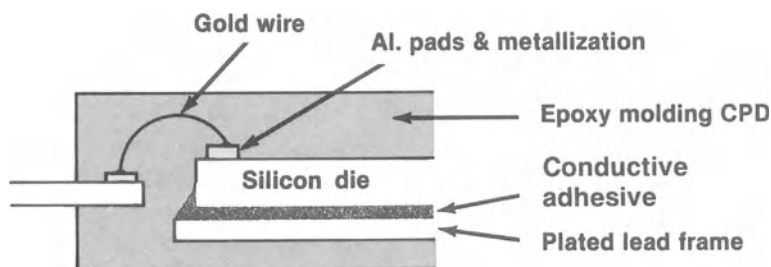
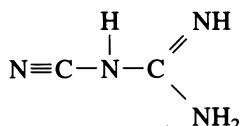


Fig. 3. Most widely used method for packaging integrated circuits—low cost plastic packages called P-DIPs (plastic dual inline packages).

purities or contaminants which may cause corrosion or other problems elsewhere in the circuit assembly. Outgassing of water or other potentially corrosive vapors is a particularly severe reliability problem in military, medical, and other high reliability circuits packaged in nonpermeable metal or ceramic packages. All organics, including all epoxies, give off water and organic vapors both during and after cure. Vapors given off during cure are primarily solvents or low molecular weight diluent resins used to reduce viscosity. If these vapors can escape to the atmosphere, volatiles released during cure pose no long-term reliability problem unless excessive use of solvent causes foaming of the adhesive or lifting of the bonded part.

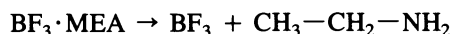
After the adhesive is cured and the die is packaged, any further release of volatiles by the adhesive is generally undesirable, particularly if the volatiles can combine with water vapor to cause corrosion. Table 3 shows two epoxy formulations which are representative of the best one-component silver-filled epoxies used for electronic assembly up to about 1980. Epoxy A in Table 3 is cured with a latent amine known as dicyandiamide (dicy):



Dicyandiamide is a crystalline, water soluble powder, which decomposes without melting at ca. 150°C. It does not react with epoxy resins at ambient temperatures but, when heated above its melting point, reacts to yield adhe-

sives with exceptionally high strength and toughness. For this reason, dicyandiamide has been used for over 30 years to make one-component epoxy paste adhesives, plus tape and film adhesives, used in aircraft assembly and in other high strength adhesive assembly operations. To permit cure at temperatures below 180°C, dicyandiamide is normally used with an accelerator, such as the chlorinated urea compound shown in Table 3. During cure, this combination of epoxy, dicy, and urea reacts to produce byproducts which include ammonia and other low molecular weight amines, and these byproducts continue to be released for long periods after cure. Ammonia plus water vapor causes alkaline attack of aluminum metallization and aluminum bonding pads.

Epoxy B in Table 3 is cured with a Lewis acid salt, the monoethylamine salt of boron trifluoride (BF<sub>3</sub>MEA). The first gold- and silver-filled one-component epoxy die attach adhesives, which were sold in the U.S. in the early 1970s, contained this curing agent. When heated to 150°C, BF<sub>3</sub>MEA liberates BF<sub>3</sub> gas, which serves as an acid catalyst to cure the epoxy.



BF<sub>3</sub> is a strong acid and, in the presence of moisture, is corrosive to aluminum and other metals. Since it is not chemically bound into the epoxy network during cure, BF<sub>3</sub> vapor can continue to be released from the cured epoxy after packaging.

The epoxy resin shown in Table 3 in Epoxy B is RDGE (resorcinol-diglycidyl ether). This was once widely used in conductive epoxies

**Table 3. Composition of First-Generation One-Component Epoxy Die Attach Adhesives.**

<i>Epoxy A</i>	<i>Weight %</i>	<i>Epoxy B</i>	<i>Weight %</i>
Epon 828 <sup>a</sup>	5.0	RDGE	27.6
Dicyandiamide	2.0	BF <sub>3</sub> MEA	0.8
Urea accelerator <sup>b</sup>	1.4	Solvent	2.8
Butyl glycidyl ether	2.8	Silver powder	68.8
Silver powder	68.8		100.0
	100.0		

<sup>a</sup>Shell Chemical Co.

<sup>b</sup>24-dichlorobenzene urea

because of its low viscosity and high strength after cure. But RDGE is now known to be a strong carcinogen, and most adhesive formulators and users now prohibit its use.

The resins, solvents and curing agents used in modern conductive epoxy adhesives are chosen to minimize residual vapors which can be released after cure. Modern epoxy adhesives generally consist of high purity Bis-A epoxies cured with a phenolic novolac resin. These mixtures do not contain boron or fluorides, and generate less ammonia or other corrosive vapors than epoxies available before 1982.

### Chlorides and Other Extractable Ionic Impurities

Ionic impurities such as  $\text{Cl}^-$ ,  $\text{Na}^+$ , and  $\text{K}^+$  can cause corrosion of Al bond pads and other metallization, loss in oxide dielectric strength in FET circuits, and other problems in high reliability (high rel) ICs. Until recently, most conductive epoxy adhesives contained very high levels of extractable chloride ions and other ionic impurities. The adhesives of Table 3, for example, would typically yield over 600 ppm  $\text{Cl}^-$  and over 200 ppm  $\text{Na}^+$ , after a 24 hour extraction in neutral water at 100°C.

Polyimide resins are inherently lower in chlorides than epoxies. For this reason, many IC manufacturers have chosen to use conductive polyimides, rather than epoxies, for high rel assembly operations, even though polyimides are more expensive, give lower bond strengths, and are more difficult to cure and to process than epoxy adhesives.

Recently, the major U.S. and Japanese resin manufacturers have made available new, highly purified epoxy resins which contain much less extractable and hydrolyzable chlorides than the best epoxy resins prior to 1980. Adhesive formulators now use these high purity epoxy resins to produce conductive adhesives, coatings, and encapsulants which yield chloride levels of 10 ppm or less and sodium levels of 5 ppm or less.

Another approach to formulating high purity

adhesives is to use an inorganic (i.e., glass) binder. Conductive glass adhesives are now being used for die attach in Cerdips (ceramic dual inline packages) and other high reliability IC products. A conductive glass adhesive typically consists of silver powder and a low melting lead borate glass powder, plus solvent, binder resins, and other additives. To form the bond, the adhesive is first dried at approximately 100°C to drive off the solvent, and then fired at 400–430°C to burn off the rest of the organics and melt the glass powder to form a permanent, completely inorganic bond. Because of the high thermal conductivity of the glass, these silver-glass adhesives have three to five times higher thermal conductivity, and up to ten times higher electrical conductivity, than the best silver-filled epoxies or polyimides.

Future production advances should result from new epoxy adhesive types that permit a variety of B-staging methods. These adhesives can be applied as a thin film, for example, on the back of the wafer before die separation, can then be B-staged to a dry, nontacky film, and later bonded directly to LED or IC substrates. Rapid cure (5–10 sec) of these B-staged adhesives can be accomplished above 300°C.

### Conductive Tape Adhesives

Another way of automating assembly is to use the epoxy adhesive in the front of a silver filled or oxide filled tape. These tapes are made by impregnating the epoxy adhesive into a glass mesh support, B-staging to form a tack-free film, and then slitting the tape into rolls or die-cutting the tape into custom-made preforms. In production, the user places a preform under the part to be bonded, or uses a machine to chop or punch preforms from a roll of tape. In either case, the tape provides precise control of bond thickness, eliminates voids, and avoids an excessive fillet. The tapes can be cured very quickly, at temperatures over 160°C, and the controlled thickness of the bond reduces thermal stresses due to thermal expansion mismatch between bonded part and the substrate.



# Structural Adhesives in the Aerospace Industry

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Adhesives are used extensively by the aerospace industry for bonding structural components of aircraft (both military and commercial), missiles, and satellites. Sealants are used in joints around windows, in fuel tanks, etc.; hot melts and pressure sensitive adhesives are utilized in aircraft interiors (primarily in fabricating decorative panels); while thermosetting adhesives are used to bond load bearing structural components.

This chapter deals exclusively with structural adhesives employed in the fabrication of load bearing components of the aircraft. In general the adhesives currently in use will meet the requirements of the Mil-A-25463 and/or MMM-A-132 military specifications. Mil-A-25463 establishes requirements for adhesives for bonding sandwich structure comprised of metal honeycomb and metallic skins, while MMM-A-132 establishes requirements for adhesives for bonding metal-to-metal airframe structure (i.e., metal skins to metal skins or metal skins to metallic spars or stringers). Both specifications define the structural requirements of adhesives having service temperature ranges of  $-67^{\circ}\text{F}$  to  $+180^{\circ}\text{F}$ ,  $300^{\circ}\text{F}$ , and  $500^{\circ}\text{F}$ . In addition, requirements for strength retention are specified after prolonged exposure to salt spray, humidity, and various aircraft fluids such as jet fuel, anti-icing fluids, and hydraulic oils.

The requirements that perhaps most clearly define the characteristics needed in a truly structural adhesive are those specifying maximum limits on creep under sustained load. MMM-A-132, for example, specifies that lap shear creep at  $75^{\circ}\text{F}$  can not exceed 0.015 inch in 192 hours under a 1600 psi load. Limits set on creep at higher temperatures help define the service temperature limitations of the specific adhesive. Similarly, Mil-A-25463 sets stringent limits on creep deflection under load on bonded sandwich structure. For all practical purposes the need for creep resistance makes it mandatory that thermosetting adhesive be utilized in aircraft structure. Thermoplastics having the required resistance to creep even at  $180^{\circ}\text{F}$  have melting points that are so high that they would be very difficult to process.

Aircraft company specifications will usually require that the adhesive meet the requirements of one or both of the military specifications. In addition, further more stringent requirements are established that are deemed critical to the particular application. For example, in the case of an adhesive used for bonding engine nacelles, requirements for strength retention after thousands of hours' exposure at temperatures of  $300^{\circ}\text{F}$  or higher would be specified. In the case of an adhesive used in a satellite, a limit would be established on outgassing under the

ultra-high vacuum conditions that prevail in a space environment.

## EVOLUTION OF BONDING IN THE AEROSPACE INDUSTRY

The first applications of adhesives for bonding aircraft structure probably date back to about 1920, when light-weight airframes were fabricated with plasticized nitrocellulose-impregnated fabric stretched over a framework of wooden stringers. The wood adhesives used for these applications were first based on casein, then urea formaldehyde resins, and finally phenol formaldehyde resins.

As aircraft structure shifted from wood to aluminum, more sophisticated adhesives capable of withstanding higher stresses were required. De Bruyne of Aero Research Ltd. in Britain is generally credited with doing the pioneering work that led to the development of the first commercially important adhesive for metal bonding. This system, known as Redux, was first used by De Havilland and Bristol in the mid-1940s. The Redux process involved applying a liquid phenolic resin to the surface to be bonded, covering the liquid with excess powdered vinyl resin, allowing the resin time to wet out, and then shaking off the excess powder. Under the influence of heat and pressure the vinyl dissolved in the phenolic resin prior to initiation of the crosslinking reaction, resulting in a bond having substantially greater toughness than that obtained with the unmodified phenolics previously used to bond wood. Fortunately, the ratio of phenolic resin to vinyl powder was reasonably noncritical, and reliable bonds could be obtained using this system.

Although Redux is still in use today, it has largely been displaced by adhesives supplied in film form. The advantages of film adhesives over the Redux system are twofold: (1) they are supplied at exactly the desired weight, and (2) the formulation is precisely controlled (i.e., the ratio of phenolic resin to vinyl resin). As a consequence the aircraft manufacturer is less dependent on the skill of the individual applying the adhesive.

Work by de Bruyne was closely followed by activity at Chance-Vought, Consolidated Vultee, and Martin. Chance-Vought explored alu-

minum skin-balsa wood sandwich structure, Consolidated studied bonded aluminum-skin-to-aluminum construction, while Martin worked with sandwich structure consisting of aluminum skins bonded to aluminum honeycomb. The types of adhesives evolved to support these activities were vinyl-phenolic, epoxy-phenolic, and nitrile-phenolic film adhesives. All of these early adhesives containing phenolic functioned via a condensation reaction, and water was evolved during heat cure. As a result very high pressure was required to minimize porosity in metal-to-metal bonds, while in sandwich structure perforated honeycomb was used to permit the escape of the condensation volatiles. In the case of honeycomb assemblies, edge sealing of the bonded panels was required to prevent ingestion of moisture, salt spray, and other hostile fluids encountered in service. If the edge seal was defective or became damaged in service, large amounts of water would be ingested into the panels as a result of altitude cycling.

The next major improvement in aerospace adhesives occurred in the late 1950s with the introduction of adhesives based on epoxy resins. Since these adhesives crosslink via an addition reaction, no volatiles are released during heat cure. This made low pressure bonding possible and the use of nonperforated honeycomb feasible in sandwich structure. Other improvements followed that resulted in more durable bonded structure. These include the development of corrosion inhibiting adhesive primers in 1968, corrosion resistant aluminum honeycomb in 1969, and the phosphoric acid anodizing process for preparing aluminum for bonding in 1974.

The most recent development is the sharp increase during the past decade in the use of non-metallic composites as structural components. These materials are prepared from so-called "prepregs" based on unidirectional or woven fabrics composed of aramid, glass, or carbon fibers, and for the most part impregnated with thermosetting epoxy formulations. To keep pace with this development, compatible adhesives have been designed that can be either (1) co-cured with the prepregs, or (2) used to bond cured composite to itself, to metallic substrates, or to honeycomb.

## ADVANTAGES AND TYPES OF BONDED STRUCTURE

The primary advantages of bonded over mechanically fastened structure are lighter weight and improved resistance to fatigue. Both of these attributes are critical to the Aerospace Industry and are responsible for the extensive use of bonding by the industry.

Bonding results in weight savings by making it possible to reduce the thickness of metal or composite sheet materials (i.e., skins, doublers, etc.). In joining materials of this type together, mechanical fasteners have an inherent disadvantage because the discontinuous nature of the joint results in local stresses at the points of attachment. This results in stress concentrations, skin buckling between attachment points, low strength in tension loading, and premature failure due to fatigue in the areas of high stress concentration at the points of attachment. The net result is that with mechanical fasteners it is not possible to design joints based on the strength properties of the thin skins. Bonded joints, because they are continuous in nature, reduce local peak stresses. This makes it possible through proper design to realize the ultimate strength properties of thin sheets.

Factors that must be considered in design are modulus of the adhesive, bond line thickness, and depth of overlap. The use of low modulus adhesives reduces peak stresses at the edge of the joint, as low modulus adhesives strain (elongate) more under applied shear stresses than do high modulus adhesives. The net result is that shear loads can be carried farther back from the edge of the joint, resulting in more uniform stress distribution. The magnitude of shear strain under an applied load is proportional to bond line thickness. Therefore, increasing the bond line thickness has about the same effect on stress distribution as decreasing adhesive modulus. Once the modulus of the adhesive and bond line thickness have been established, the designer is in a position to decide on the appropriate bond line overlap depth because he now knows how far back into the joint the applied load will be carried. The optimum depth of the joint will, of course, also depend on the modulus and thickness of the substrates.

It should be apparent from the above discus-

sion that stiffness (i.e., high modulus) is an undesirable trait in an adhesive for most applications. As a general rule the adhesive modulus should be as low as possible consistent with resisting creep under the applied load. Since both heat and absorbed moisture reduce the modulus of adhesives, data on the modulus at the maximum service temperature under wet conditions will be required before selection of an appropriate adhesive. This subject is discussed in much greater detail in two papers by R. B. Krieger.<sup>1,2</sup>

Another type of bonded structure in common use by the aerospace industry is the honeycomb sandwich panel, consisting of thin skins bonded to a hexagonal honeycomb core. This type of structure is very weight efficient, as it has an extraordinarily high stiffness-to-weight ratio. There is no economical way of fabricating structures of this type except by bonding. Fig. 1 depicts a section of a honeycomb sandwich panel. Design flexibility on this type of panel is practically unlimited. Thickness of skins, thickness of honeycomb, diameter of the hexagonal cells, honeycomb foil gauge, and thickness of the facing adhesive can all be varied to meet specific design requirements. Moreover, additional skins, doublers, spars and various other types of reinforcements can be bonded into areas subjected to high stress levels. The efficiency of honeycomb structure derives from the fact that most of the weight is concentrated in the skins at the top and bottoms of the panel, where it is most needed to carry tension and compression loads. In addition to preventing buckling by stabilizing the skins over their entire surface, the honeycomb serves to uniformly transmit shear loads to the skins. As was

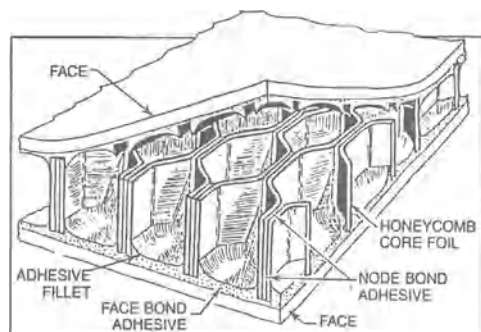


Fig. 1. Honeycomb sandwich construction.

the case with skin-to-skin bonds, the elimination of localized stress concentrations caused by mechanical fasteners permits the fabrication of very light weight panels having excellent resistance to fatigue. Honeycomb is available in densities ranging from less than 2 lb to over 40 lb per cubic foot to withstand the shear loads required by specific designs.

The skin-to-skin bond and the honeycomb sandwich bond can involve either metallic or nonmetallic composite substrates or a combination of the two. Bonding is a very attractive method of joining composite materials because their ability to withstand local stresses caused by mechanical fasteners is quite poor when compared to metals. This is especially true of composites in which the fiber orientation is unidirectional in order to increase stiffness along a specific axis.

In the case of bonded high modulus composites, failure at low load levels due to interply delamination within the composites is a common problem. The use of low modulus adhesives minimizes this problem.

High modulus composites designed for high temperature service tend to have relatively low impact strength. Dramatic improvements in impact strength can be achieved through the use of so-called interleaf films. These are based on zero flow, low modulus adhesives that will not mix with the composite prepreg during cure. Since there is no intermixing, the modulus of the prepreg resin is not reduced and the stiffness of the structure is preserved.

A final use of adhesives for composite structure is as a surfacing ply. In this application a low flow adhesive is applied to the composite surface prior to cure in order to produce a cosmetically smooth surface that is ready for painting without further finishing operations. In addition, surfacing ply adhesives as well as interleaf films have been effective in reducing the porosity of composite skins. This has led to their applications in "wet wings" to prevent fuel leakage and in composite skin sandwich structure to prevent moisture penetration.

Composite bonding and the use of interleaves to improve impact resistance are discussed in more detail in papers by R. E. Politi and K. R. Hirschbuehler.<sup>3,4</sup>

## EXAMPLES OF BONDED STRUCTURE

Figure 2 gives some indication of the degree to which bonding is utilized in a modern aircraft. Body skins and tear straps account for most of the bonding on the fuselage. The interior floor panels consist of skins bonded to honeycomb core. Access doors and bulkheads are also bonded. Flaps, spoilers, and leading edge slats on the wings and empennage are bonded. Engine struts as well as acoustic engine cowl panels are also bonded.

Honeycomb details used in a bonded acoustic engine nacelle are shown in Fig. 3. The final assembly will have solid outer skins but the inner skins will be perforated in order to reduce noise levels.

Figure 4 illustrates a bonded honeycomb helicopter blade. This application requires the ultimate in fatigue resistance. Some of the early blades made with mechanical fasteners had fatigue lives of less than 100 hours. Bonding reduced stress concentrations to the point that fatigue life now exceeds several thousand hours. The steel spar bonded into the leading edge of the blade contributes to its rigidity as well as making it more capable of withstanding impact loads. Multiple layers of bonded doublers at the root end of the blade serve to reinforce it where flexure stresses are the greatest.

Finally, Fig. 5 is a cross section of a typical honeycomb sandwich trailing edge wing flap. Note the use of high density honeycomb to reinforce the area adjacent to the spar caps used for attachment to the main wing structure.

## PHYSICAL FORMS OF ADHESIVES

Although film adhesives account for the overwhelming bulk of structural adhesive used by the aerospace industry, expandable and syntactic adhesive foams, paste adhesives, and adhesive primers are all necessary parts of a complete bonding system.

Film adhesives are usually supplied coated on nonstick release paper. Depending on the tack level of the specific adhesive, a polyethylene liner may also be utilized. Most but not all film adhesives contain a fabric carrier. This carrier makes the adhesive less fragile during handling and also serves as a means of con-

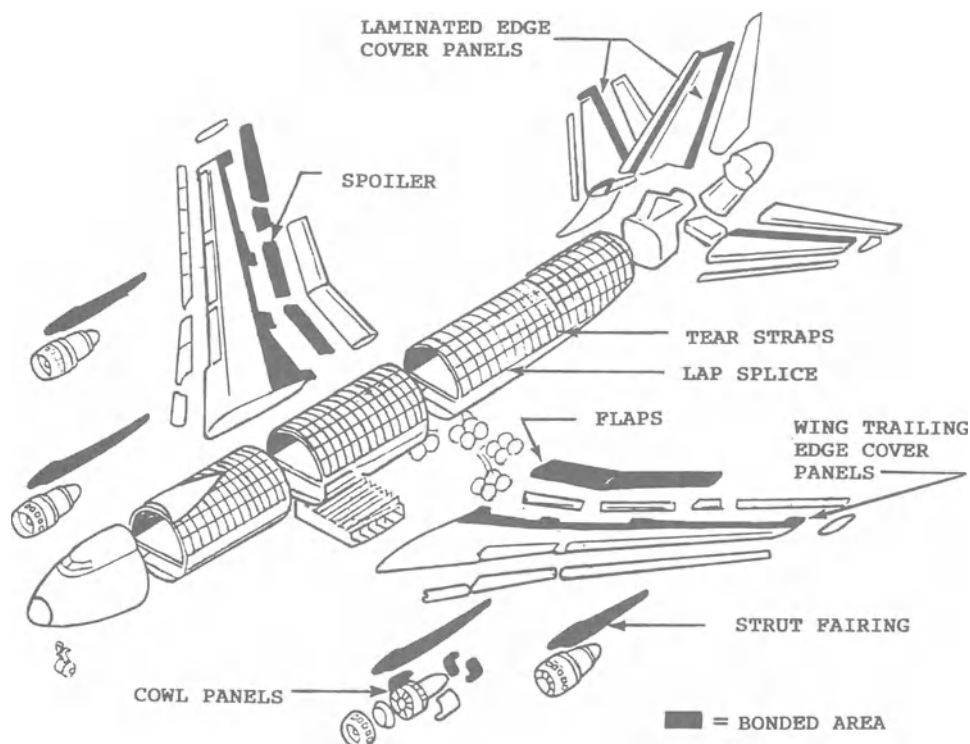


Fig. 2. Schematic showing bonded areas. (Courtesy Boeing Co.)

trolling the thickness of the bond line. In the early years of bonding, cotton and nylon fabrics were frequently used as carriers. In order to improve resistance to high humidity conditions, most of the adhesives developed during the past 10–15 years are supported by more water resistant fabrics based on fiberglass or polyester fibers. Depending on the handling characteristics required, tack levels can vary from nontacky to aggressively tacky.

Thickness of the adhesive is varied to suit the specific application. For example, when the substrates to be bonded are smooth and uniform in thickness a light weight adhesive of about 5 mils in thickness is usually selected. For assemblies having large or variable gaps, adhesives up to 15 mils or higher in thickness are utilized. Examination of the honeycomb panel pictured in Fig. 1 makes it obvious that adhesive thickness is a critical factor that must be considered in the design of sandwich structure. The size of the adhesive fillets and thickness of the face bond adhesive determine the

depth to which the honeycomb core foil penetrates into the face bond adhesive. This in turn dictates how great a shear load the adhesive is capable of transferring to the face sheets. For very light weight sandwich panels used in the construction of satellites or other lightly loaded structure, very light weight adhesives are suitable. For heavily loaded panels fabricated with relatively thick face sheets and high density honeycomb, thicker and heavier adhesives are required. It should also be apparent from Fig. 1 that precise control of flow of the adhesive is required. The adhesive must flow sufficiently to give good fillet formation but must not run down the honeycomb cell walls from the top face.

Expandable foams are used to splice pieces of honeycomb together or to splice the honeycomb to edge members of the sandwich panel. These foams expand prior to gelation during heat curing. Low density high expansion foams are suitable for lightly loaded structure, while lower expansion foams of 30–40 lb per cubic

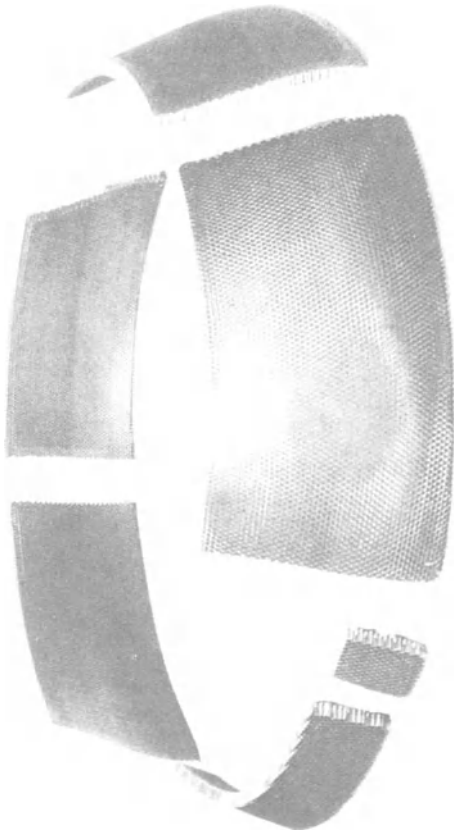


Fig. 3. Honeycomb engine nacelle details.

foot density are used in heavily loaded structure.

Syntactic foams are generally supplied in paste form as either one-part heat cure or two-part room temperature cure systems. These systems usually contain hollow glass microspheres, and most commonly have densities in the 40 lb per cubic foot range. The major use of these paste foams (also known as potting compounds) is to provide local reinforcement of honeycomb panels where mechanical fasteners such as threaded bolts are to be inserted in order attach the bonded panel to another part

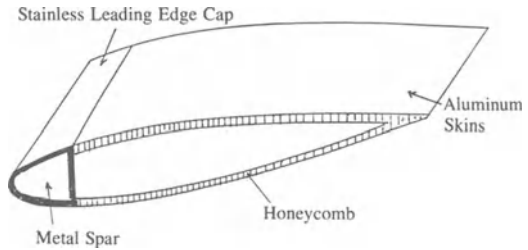


Fig. 4. Bonded helicopter blade.

of the aircraft structure. The cross section of a sandwich panel shown in Fig. 6 illustrates how syntactic foam is used to provide better holding power for a threaded fastener.

Syntactic foams are also available in sheet form, generally at thicknesses of 20–40 mils. Since it is impractical to machine conventional honeycomb down to this thickness range, this form of syntactic foam has found use in very thin sandwich structure fabricated with composite skins.

Aerospace paste adhesives are usually thixotropic in nature. A major use is as a gap filler in areas where the mismatch is so great that the use of film adhesives becomes impractical. Other uses are in joints where pressure cannot easily be applied or as high density potting compounds where syntactic foams do not provide sufficient strength. Pastes are also utilized as fairing compounds in areas such as wing-to-engine pylon joints to provide aerodynamic smoothness in order to reduce drag in flight. Both one-part heat cure and two-part room temperature cure pastes are utilized by the industry.

Adhesive primers are an integral part of a complete adhesive system. Although it is possible to obtain excellent adhesion to casually cleaned (e.g., solvent wiped) metals, these bonds are seldom durable when exposed to hostile environments such as salt spray or 100% humidity conditions. In the case of aluminum,

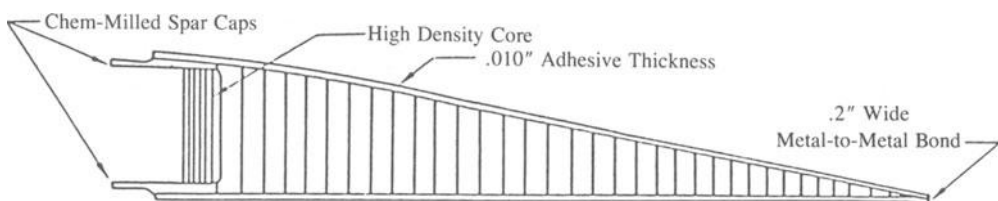


Fig. 5. Trailing edge flap.

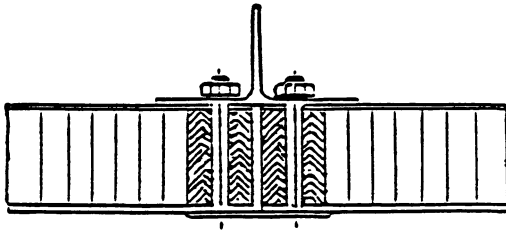


Fig. 6. Potting compound used for local reinforcement of honeycomb.

titanium, and many other metal alloys, special treatments are required to provide a stable bonding surface. Aluminum alloys such as 2024-T3 and 7075-T6 account for most of the bonded metallic structure in aircraft and this discussion will be limited to primers for these alloys.

Three surface treatments for aluminum are in wide use: (1) chrome-sulfuric acid etching, (2) chromic acid anodize, and (3) phosphoric acid anodize. All of these impart a controlled oxide layer to the surface of the aluminum that is suitable for bonding. Unfortunately these oxide layers will hydrolyze if the panels are stored for prolonged periods of time. One function of an adhesive primer is to prevent hydrolysis of these oxide layers. Most aircraft companies specify that the surface treated metal must be primed within 8 hours. In reality the actual safe storage time is inversely proportional to the relative humidity. Under extremely low humidity conditions storage times of several days do no apparent harm. However, since bond shop humidity limits are generally set at a maximum of 65% RH, limiting the time between surface treatment and priming to 8 hours appears to be prudent.

Many of the primers developed during the past 20 years contain corrosion inhibitors. These primers have a second function: to further improve hydrolytic stability at the adhesive to metal interface and prevent corrosion during exposure to salt spray. Table 1 shows the difference in strength retention of 2024-T3 alclad aluminum lap shear coupons exposed to salt spray. Both sets of coupons were bonded with a 250°F cure elastomer modified epoxy adhesive. One set of coupons was primed with BR® 123 primer (a non-corrosion inhibiting primer) while the other set was primed with

Table 1. Effect of Salt Spray on Strength Retention.

Exposure Time	Lap Shear, psi	
	BR® 123 Primer	BR® 127 Primer
Initial	5875	5680
30 days	3490	5890
90 days	1460	4970
180 days	0	4480

BR® 127 corrosion inhibiting primer. Both primers are manufactured by the American Cyanamid Company.

The data show that in the case of the BR® 127 corrosion inhibiting primer approximately 80% of the initial strength is retained after 180 days' exposure. In the case of the BR® 123 there is no residual strength after 180 days, with all of the loss due to bond line corrosion.

It should be pointed out that alclad aluminum, because of the sacrificial nature of the clad coating, is much more susceptible to bond line corrosion than bare alloys. For example, in similar tests run with 2024-T3 bare aluminum, the differences in performance between BR® 127 and BR® 123 are much less pronounced, with retentions of original strength after 180 days exposure being about 95% and 70%, respectively.

## CHEMICAL TYPES OF ADHESIVE

As previously pointed out, film adhesives account for the major share of structural adhesives consumed by the aerospace industry. Therefore, this discussion of chemical types of adhesive, after making some general comments on other types, will be limited to film-type adhesives.

In most cases the resins, curing agents, etc., used in adhesive foams are similar to those used in film adhesives. Expandable adhesive foams will obviously differ in that they will contain a blowing agent, while syntactic foams will contain hollow microballoons to reduce density. One-part heat cure pastes will contain liquid resins instead of solid resins. Two-part room temperature cure epoxy paste adhesives are generally cured with active amine curing agents, while one-part epoxy pastes, adhesive

Table 2. Structural Properties of Various Types of Film Adhesives.

Adhesive Type	Cyanamid Designation	Lap Shear at Indicated Temp., ksi								Metal Peel, lb/in. width	Sandwich peel, in. lb/in. width
		-67°F	75°F	180°F	250°F	300°F	350°F	400°F	500°F		
Two-phase toughened Epoxy	FM® 73 (0.085 psf)	6	6	4	1.5	—	—	—	—	70	40
	FM® 87 (0.085 psf)	6	6	4	3	—	—	—	—	70	40
	FM® 300 (0.10 psf)	5	5	4.5	4	3	—	—	—	30	20
Nitrile-epoxy duplex	FM® 61 (0.075 psf)	3.5	3	2.8	—	2.7	1.6	—	—	15	25
Nylon-epoxy	FM® 1000 (0.08 psf)	7	7	3.5	2.2	—	—	—	—	140	80
Vinyl-phenolic	FM® 47 (0.075 psf)	3.5	4.5	4	2	—	—	—	—	10-15	20
Vinyl-epoxy	FM® 96 (0.075 psf)	3	3.7	4	4	2.5	1.4	—	—	10-15	15
High temp. epoxy	FM® 400 (0.10 psf)	4	4	—	—	—	2.8	2	0.8	10	15
	FM® 350 NA (0.10 psf)	4	4	—	—	—	3.5	—	—	10	8
	FM® 355 (0.10 psf)	3.3	3.1	—	3.6	—	3.2	2	—	10	8
Nitrile-phenolic	FM® 238 (0.05 psf)	4	4	3	2.5	1.7	—	—	—	70	—
Epoxy-phenolic	HT® 424 (0.135 psf)	3.2	3.5	—	—	2.7	—	—	2	< 10	10
Bismaleimide	FM® 32 (0.10 psf)	2.8	2.8	—	—	—	3	3	2	< 10	6
Addition reaction polyimide	FM® 35 (0.135 psf)	3	3	—	—	—	3	—	2.7	< 10	6
Condensation reaction polyimide	FM® 36 (0.10 psf)	3	2.8	—	—	—	2.7	—	2.7	< 10	7



foams, and film adhesives favor the use of latent amines.

Table 2 lists the major types of film adhesives in use today together with typical mechanical properties. Because many types of peel and shear tests are in use by industry, in order to avoid confusion the specimen configuration of each of the tests referred to in this table is illustrated in Figs. 7, 8, and 9. Most of the adhesives shown in this table are available in various weights and thicknesses. The data in Table 2 are representative of the heaviest weight adhesives commonly in use for each type. Lap shear and metal peel values do not vary much with weight, but sandwich peel values would be considerably lower for lighter weight adhesives. Comments regarding service temperature apply to heavily loaded structure and take into account degree of creep under sustained load. In many cases these adhesives are suitable for use at higher temperatures in lightly loaded structure.

In every case the properties shown apply to a specific American Cyanamid adhesive, because the author is most intimately familiar with that product line. Since Cyanamid offers a very

complete product line, this has not limited the coverage of this subject. In most but not all cases similar adhesives are available from other sources.

### Vinyl-Phenolic

This was one of the earliest types of structural adhesive used by the aerospace industry. Vinyl-phenolics are still in use today because they are reasonably low in price and are excellent for applications involving bonding metal skins to wood. FM® 47 adhesive is representative of this type. The major disadvantage of this type is that crosslinking occurs via a condensation reaction. As a consequence the volatiles given off during heat cure result in porous bond lines. This type of adhesive may be stored at room temperature and is cured at 350°F. Service temperature is limited to slightly above 180°F.

### Epoxy-Phenolic

This type of adhesive also cures via a condensation reaction. Therefore, as was the case with vinyl-phenolics, volatiles evolved during cure complicate processing. A major advantage of this type of adhesive is that excellent strength at high temperature can be obtained with cure temperatures as low as 250°F. Oxidative stability during long term exposure at high temperatures is relatively poor, but strength retention after short time exposure to temperatures as high as 1000°F is excellent. For this reason this type of adhesive has been extensively used in bonding on missiles. This system has limited stability at room temperature, and shipping and storage at 0°F is recommended.

### Nitrile-Phenolic

These adhesives are used exclusively for sheet-to-sheet bonding because they are extremely low flow and are not suitable for bonding to honeycomb. Strength retention is good up to 250°F and fair at 300°F. Metal peel is excellent at room temperature. However, the glass transition temperature is relatively high, resulting in poor metal peel at low temperatures. Recommended cure temperature is 350°F. Because of their low flow, high pressure bonding

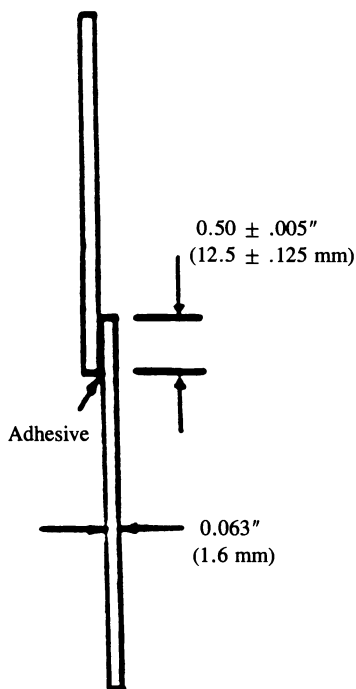


Fig. 7. Lap shear specimen.

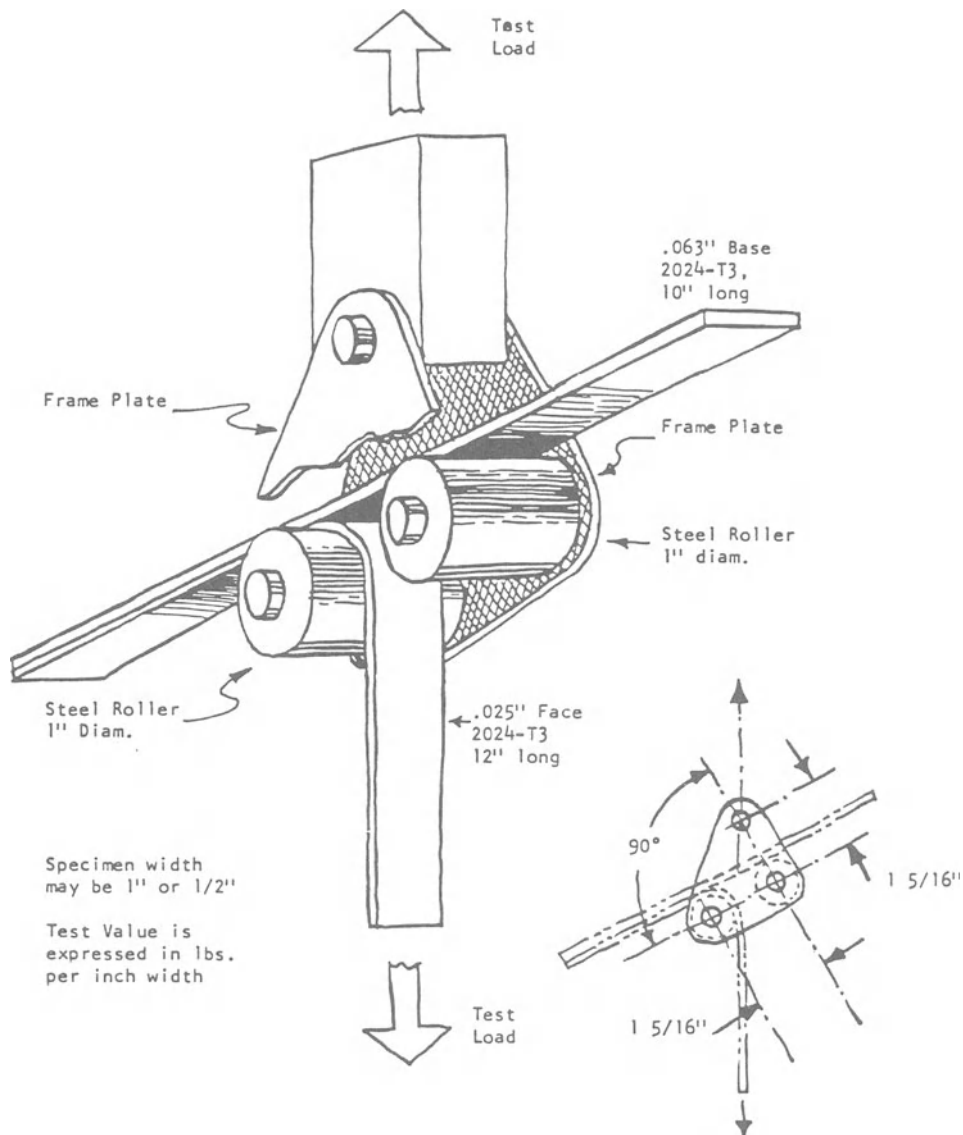


Fig. 8. Floating roller metal peel.

(100 psi +) is required for optimum performance.

### Early Epoxy Adhesives

Aerospace adhesive manufacturers were quick to exploit epoxy resins. Starting in the early 1950s, a succession of epoxy and modified epoxy adhesives were developed and commercialized. The major advantage of epoxy based adhesives was that crosslinking occurs via an addition reaction. As previously stated this made low pressure bonding possible and permitted the use of nonperforated honeycomb.

### Vinyl-Epoxy

FM® 96 is one of the early adhesives that is representative of this type. It has moderate strength at temperatures up to 300°F. Oxidative stability is excellent which led to its use in areas of the engine nacelle and other hot spots where continuous exposure to temperatures up to 300°F are involved. Some improvement in toughness over unmodified epoxies is achieved through modification with a high molecular weight vinyl resin. As a result moderate metal peel and sandwich peel values can be achieved. This type of adhesive can be shipped and stored

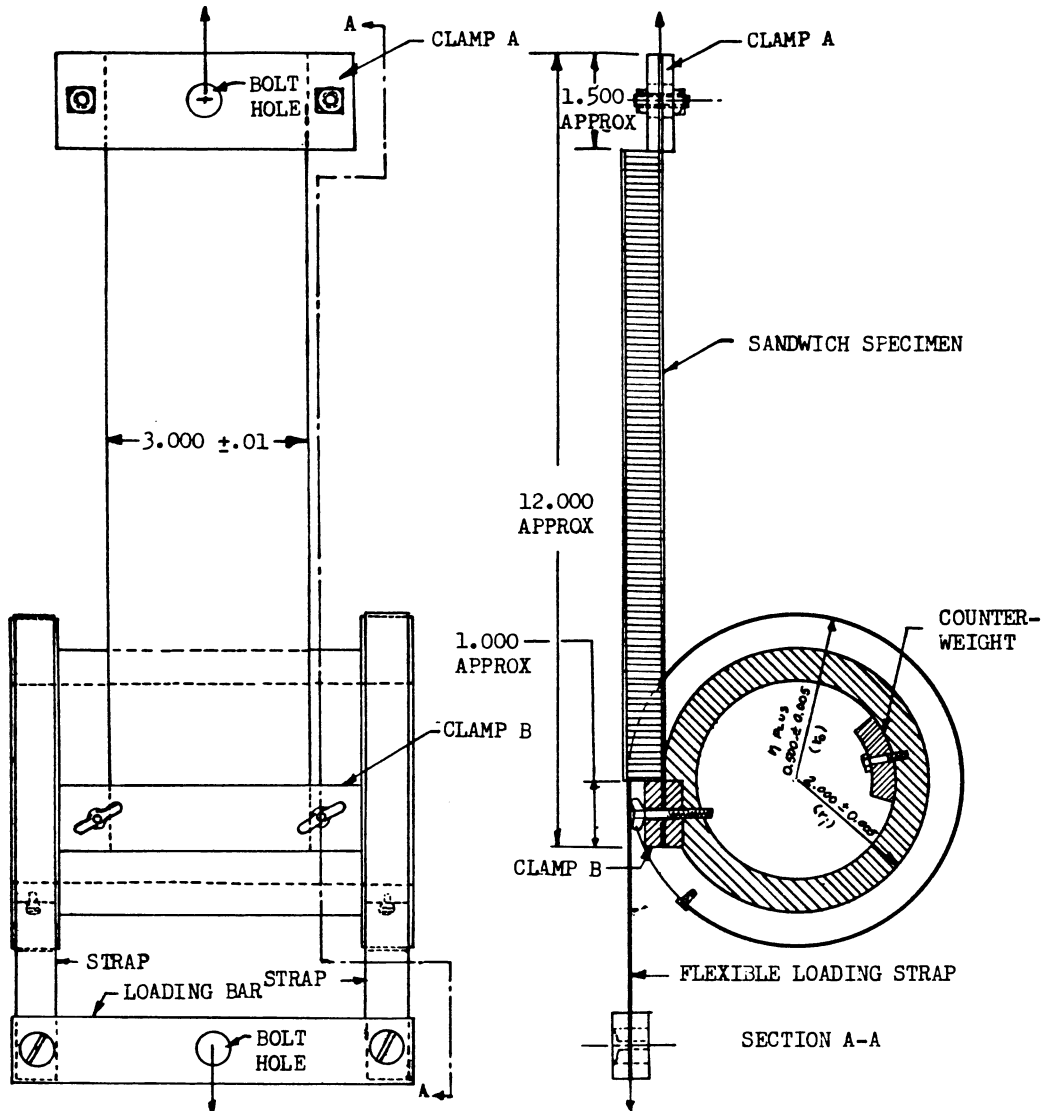


Fig. 9. Honeycomb climbing drum test fixture.

at room temperature. Cure temperature is 350°F.

### Nitrile-Epoxy Duplex

This type of adhesive, exemplified by FM® 61, consists of a high flow epoxy layer coated over a low flow nitrile-epoxy layer. In sandwich panels the high flow epoxy side is placed against the honeycomb and gives excellent fillet formation, while the low flow rubber epoxy side placed against the skin enhances peel. Metal peel is fair, while sandwich peel values are fairly high. Strength retention is good at

temperatures up to 300°F. This adhesive is stable at room temperature. Recommended cure temperature is 350°F.

### Nylon-Epoxy Adhesives

Nylon-epoxy adhesives are the toughest class of structural adhesive available. Lap shears in excess of 7000 psi are obtainable. Sandwich and metal peel values are also extremely high about 140 in. lb/in. and 80 lb/in., respectively. Because of the high concentration of nylon this adhesive is quite susceptible to plasticization by absorbed moisture. For this reason, perfor-

mance under long term sustained loads at high humidity and elevated temperatures (e.g., 100% RH and 140°F) is not as good as most other types of epoxies. Nevertheless this type of adhesive has proved to be extremely durable in properly designated structures and is unsurpassed in resisting constant fatigue stresses. Recommended cure temperature is 350°F and the service temperature limit is 180°F. This adhesive film may be stored at room temperature.

### More Recent Epoxy Adhesives

Over the past two decades significant advances have been made in developing epoxy based adhesives having improved performance. These improvements were made possible by (1) the discovery of unique methods of toughening adhesive and (2) the availability of new multifunctional epoxy resins.

The toughened epoxy adhesives previously discussed are single-phase systems in which the crosslinked epoxy resin is plasticized by a compatible elastomer. Because these are single-phase systems the glass transition temperature ( $T_g$ ), which is roughly equivalent to the softening point, will fall somewhere between the

$T_g$  of the epoxy and that of the elastomer. The exact  $T_g$  of the adhesive will depend on the ratio of elastomer to epoxy and their relative  $T_g$ 's. Since some elastomers have  $T_g$ 's below 0°F, the  $T_g$  of highly modified systems can be sharply reduced, the net result being a significant reduction in the ability of the adhesive to withstand high temperatures.

Current toughening technology involves blending the epoxy with an initially compatible elastomer that precipitates into small, uniformly dispersed particles during the cross linking reaction. Fig. 10 is a photomicrograph illustrating such a two-phase system. Since the high softening point epoxy is the continuous phase, the  $T_g$  of the adhesives remains unchanged, while the dispersed elastomer particles lower the modulus and toughen the adhesive. It is theorized that toughness and peel are improved because the ductile dispersed particles stop crack propagation initiated by applied stresses.

The earliest epoxy adhesives were based on difunctional bisphenol resins. As the epoxy manufacturers introduced more functional resins, first the epoxy novolacs and then a series of high functionality specialty resins, aero-

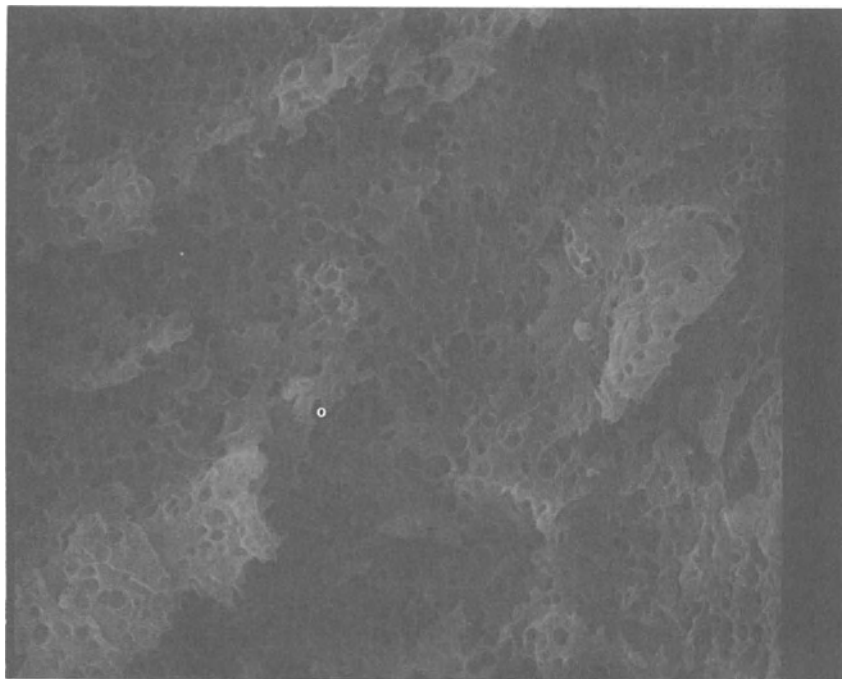


Fig. 10. Two-phase toughened epoxy.

space adhesive manufacturers were able to utilize them in formulating adhesives having higher service temperatures. In many cases these high temperature adhesive are two-phase toughened systems containing dispersed elastomers.

### Two-Phase Toughened Epoxies

These adhesives currently account for a major share of structural adhesives consumed by the aerospace industry. FM® 73 and FM® 87 are representative of 250°F cure adhesives of this type that have service temperature limits of 180°F and 250°F, respectively. Both adhesives have controlled flow and have excellent metal peel and sandwich peel. FM® 300 is a 350°F cure adhesive having good strength retention up to an operating temperature of 300°F. Contrasting it with a single-phase system such as FM® 96 makes the advantages of a two-phase system obvious; FM® 300 has better 300°F strength and higher metal and sandwich peel (both toughness related properties). Because of this balance of properties and its controlled flow, this adhesive has been extensively used for bonding composites and as a surfacing ply to impart smoothness and reduce porosity. A zero flow version of this adhesive is effective as an interleaf material to improve the impact resistance of composite structure.

All three of these adhesives must be kept at 0°F for extended storage periods. Storage up to about 10 days at a maximum shop temperature of 90°F during processing is permissible.

### High Temperature Epoxies

The properties of three high temperature epoxy adhesives are summarized in Table 2. FM® 400 is a high temperature adhesive containing aluminum powder as a reinforcing filler. This adhesive has excellent strength retention at temperatures up to 400°F. However, oxidative stability at this temperature is not outstanding. For this reason the major application for this type of adhesive is in high speed military aircraft rather than in engine nacelles where long term exposure to high temperatures is required. Metal peel values are modest while sandwich peel values are fairly high.

FM® 355 also has good strength retention at

400°F. It is an unfilled adhesive and, therefore, is suitable for applications requiring radar transparency. This type of adhesive has also found application in bonding high temperature composites.

FM® 350 NA is a 350°F curing adhesive with good strength retention at 350°F and excellent oxidative stability. For this reason it is suitable for engine nacelle applications involving thousands of hours exposure to temperatures of 300–350°F. An unsupported version of this adhesive is available that can be reticulated (i.e., heat shrunk) on honeycomb core. This process results in the adhesive forming a bead on the honeycomb cell edges. The honeycomb can then be bonded to perforated metal skins without plugging up the holes. This type of structure is used to fabricate acoustic panels used in engine nacelles to absorb sound and thereby meet FAA standards for permissible noise levels.

Both FM® 355 and FM® 350 NA adhesives are two-phase systems. As a result, even though metal peel and sandwich peel are modest, they are higher than those obtainable with unmodified high temperature epoxies.

### Bismaleimides

BMI adhesives are suitable for long term exposure to temperatures up to 400°F and short term exposure up to 450°F. They have excellent electrical properties, making them especially suitable for high energy radomes. Systems currently available are quite rigid and for this reason have low metal peel and sandwich peel properties. They are addition reaction systems, so no volatiles are given off during cure. This simplifies processing and makes possible nonporous bondlines with low bonding pressures. These systems are usually cured for several hours at 350°F under pressure and then postcured at 400–450°F with or without pressure.

### Polyimides

Two types of polyimides (PIs) are currently in use. Condensation PIs were the first type introduced. They are based on the reaction product of aromatic diamines and aromatic dianhydrides, and are capable of withstanding pro-

longed exposure to temperatures of 500–600°F and short term exposure to temperatures up to 1000°F. In addition to the condensation volatiles, processing is further complicated by the presence of high boiling solvents needed to make the adhesive pliable and capable of flow. To facilitate removal of volatiles these adhesives are generally processed under high vacuum conditions. Condensation PIs can be cured under pressure at 350°F. After about two hours at 350°F they develop sufficient green strength to permit post curing at 500–600°F without pressure.

Addition reaction PIs are also based on aromatic diamines and dianhydrides, but in addition have Nadic imide end groups. These systems also contain solvents to make the adhesive film pliable. Curing of these adhesives initially proceeds via a condensation reaction at low pressure. However, unlike the conventional condensation reaction PIs, after completion of the condensation reaction and removal of solvent, these adhesives are still thermoplastic. At this point the temperature and pressure are increased to densify the bond line and the  $T_g$  is increased via an addition reaction through the Nadic end groups. Typical processing conditions are (1) heat from room temperature to 400°F in 1 hour under light contact pressure; (2) hold 30 minutes at 400°F; (3) increase pressure to 100 psi and increase temperature to 550°F, hold at 550°F for 2 hours. This processing method results in void-free bonds.

The oxidative stability of addition reaction PIs is not quite equal to that of the condensation type. For prolonged exposure about 500°F is the limit, but short term strength retention is good up to 600°F.

PI adhesives have excellent electrical properties and are suitable for high temperature radomes. They are also used in very hot areas of engine nacelles.

## PROCESSING CONSIDERATIONS

This section describes processing procedures and some of the more important factors that impact on the quality and durability of bonded structure. Topics covered include (1) surface preparation, (2) proper storage and handling,

(3) control of bond shop environment, (4) control of bonding process, and (5) verification of quality of the adhesive bond.

## Surface Preparation

A wide variety of substrates are utilized by the aerospace industry in fabricating bonded structures. These include aluminum, stainless steel, and titanium alloys as well as thermosetting and thermoplastic composites. Most metallic substrates are prepared for bonding by immersing them in caustic and/or acidic solutions to remove mill oils, etch the surface, and in some cases deposit a controlled oxide layer. In the case of aluminum, which is the most widely used metal, the most commonly used surface preparation methods are chrome-sulfuric acid etching, chromic acid anodizing, and phosphoric acid anodizing. Nonmetallic substrates, depending on their specific composition, may be grit blasted, sanded, roughened through the use of a removable peel ply, etched with acids or bases, flame treated, plasma etched, etc. Details on suitable surface treatments for widely used substrates are generally available from the adhesive suppliers.

In the case of metal substrates primers are usually applied to protect the surface from contamination and hydrolysis as well as to enhance the durability of the bond. Primers are usually spray applied. Depending on the specific primer the thickness can vary from 0.1 to 2 mils. Prior to application of the adhesive, the primer is air dried or heat dried to remove solvents and in some cases heat cured.

As a class, high peel elastomer modified epoxy adhesives are very dependent on primers. Initial bond strength to metals can be excellent without primer, but durability in a humid environment will invariably be poor. For example, lap shear specimens of FM® 73 bonded to unprimed titanium failed in about 3 days under a 1000 psi load at 140°F and 100% RH. Specimens primed with BR® 127 primer did not fail after being subjected to these conditions for 1 year.

Contamination of the surface, improperly maintained acid solutions, inadequate rinsing, and other factors can also result in adhesive

bonds having poor durability under humid conditions. An accelerated test that is effectively used by many aerospace companies to verify that surface preparation has been adequate to insure durability is the *wedge test*. In this test a wedge is driven between two strips of bonded substrate material. After allowing the specimen to stabilize for one hour the crack length is recorded and the specimen is placed in a cabinet maintained at 140°F and 100% RH for one hour. Crack growth under these conditions should be very slight and should be primarily due to cohesive failure rather than failure between the adhesive and the substrate. Fig. 11 illustrates a wedge test specimen frequently used in process control for bonded aluminum structures. (The technique is, of course, applicable to other substrates).

### Storage and Handling

Most structural adhesives are based on polar resins and, therefore, will absorb moisture when exposed to humid conditions. For this reason, the rolls of adhesive are packaged in vapor barrier bags to prevent moisture absorption during shipping and storage. In the case of adhesives that are stored at 0°F, the rolls should be thawed out for about 16 hours before removing the vapor barrier bag in order to avoid condensing water on the surface of the adhesive.

The need to avoid exposure of the adhesives to high humidities is well recognized by the industry, and for this reason the humidity in most bond shops is not allowed to exceed 65% RH. Less well recognized is the need to limit the exposure to humidity of certain types of composite substrates during storage prior to bonding. Relatively small amounts of moisture absorbed by these substrates will vaporize dur-

ing high temperature bonding, resulting in porous bond lines.

### Bonding Procedures

Flat panels of uniform thickness are frequently bonded in heated platen presses. However, most bonded aerospace assemblies are contoured. For this reason, bonding is usually carried out in heated, pressurized autoclaves. In the autoclave process the assembly is supported by a tool of the required contour, wrapped with several layers of glass or polyester bleeder cloth, and then enclosed in a impermeable heat resistant bagging film. This layup is then placed inside a pressurized autoclave and the inside of the bag is vented either to the atmosphere or connected to a vacuum pump. The autoclave is then pressurized to the desired level by compressed air, nitrogen, or other relatively inert gas.

The function of the bleeder cloth is to absorb adhesive flash and provide an unrestricted path so that entrained air or reaction volatiles can be removed. In the case of condensation reaction polyimides the bag should be vented to relatively high vacuum conditions. This is critical because it is necessary to depress the boiling point of the high boiling point solvents used to flexibilize the film before gellation of the adhesive occurs.

Heatup rates may be anywhere from 1 to 10°F per minute to the final bond temperature. Slow heatup rates are sometimes specified for assemblies having variable thickness in order to maintain uniform temperatures throughout the bond cycle and thereby minimize heat distortion and locked-in thermal stresses.

Bonding pressures of about 40 psi are employed with most addition reaction adhesives. However, pressures as low as 15 psi may be used with some light weight sandwich panels to prevent crushing the honeycomb, while 100 psi pressure may be used in bonding large body skins together in order to reduce voids by compressing any entrained air. The use of nontacky or one-side tacky adhesives has been found to be effective in reducing voids in large area skin-to-skin bonds. By pulling vacuum on the as-

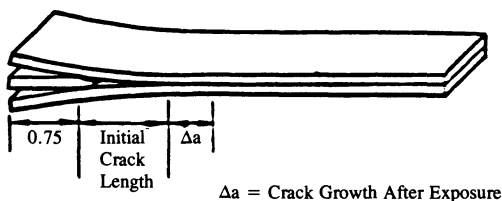


Fig. 11. Wedge test specimen.

sembly to remove entrained air, voids can be virtually eliminated.

### Verification of Bond Quality

In order to verify that the bonding process is under control, process control panels are frequently bonded along with the production assemblies and then tested to determine bond strength. Lap shear, metal peel, or sandwich peel panels are the type most frequently used for this purpose.

The bonded assemblies are then subjected to nondestructive tests designed to determine the presence of voids. Some adhesives are formulated to be x-ray opaque in order to simplify void detection. Tapping the surface with a coin will detect very large voids. However, this

method has been largely displaced by sophisticated devices capable of detecting very small voids through the use of ultrasonic sound waves.

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# Adhesives in the Automobile Industry

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The automotive use of adhesives is nearly as old as the industry itself. The early wood and canvas bonding agents have been replaced by formulations capable of holding metal, glass, plastics, rubber, and a variety of fabrics to themselves, to each other, and to painted surfaces. They are routinely used in structural, holding, and sealing applications. Automotive adhesives have become increasingly sophisticated and capable over the past twenty years. This trend has been driven by a need to bond new weight-saving and/or corrosion-resistant materials in an ever more health and cost conscious environment. The most significant trends since the previous edition of this Handbook have been the increased use of plastics and galvanized steel, a shift toward the robotic application of adhesives and sealants, and the use of nondestructive testing and statistical quality control techniques.

## UNIQUE AUTOMOTIVE REQUIREMENTS

Automotive adhesives must meet a number of requirements which are more or less independent of joint performance. They must be usable under conditions which include:

1. A largely unskilled workforce, often with a high turnover rate.
2. High production rates (some lines are designed for 100 cars per hour) with short, unvarying times for each operation.
3. Minimal cleaning of surfaces, which are subject to sudden or gradual contamination.
4. Low tolerance for health and safety hazards.
5. Cure times, pressures, and temperatures which are somewhat variable and which may need to be compatible with paint bake schedules or low material heat distortion temperatures.
6. A desire to avoid complex measuring and mixing.

Once these requirements have been met and the joint is made, adhesive bonds must perform for the life of the car under severe conditions. No other mass produced product approaching the complexity of a modern automobile is expected to function from  $-40^{\circ}\text{C}$  ( $-40^{\circ}\text{F}$ ) to over  $90^{\circ}\text{C}$  ( $200^{\circ}\text{F}$ ), endure exposure to changing temperatures, salt water, fuel, oil, high humidity, vibration, impact, detergents, and dust. Adhesives have been able to meet these requirements and do it with life-of-the-car durability, a real tribute to both the automotive and the adhesives industry.

## STRUCTURAL ADHESIVES

Structural adhesives, for the present purposes, may be defined as those which transmit significant mechanical loads. They are typically thermosetting and are generally epoxies, phenolics, polyurethanes, polyesters, or some variation thereof, although certain plastisols are an important exception.

Structural adhesives have come into use because they reduce stress concentrations, provide smooth contours, increase service life or performance, or because they are the only structural assembly method available at reasonable cost. Table 1 lists the common automotive uses of structural adhesives. The resins listed are generic and may be modified from time to time at the request of the supplier or the user.

One of the oldest applications listed in Table 1 involves bonding hood inner and outer panels. Automotive hoods and roofs have a tendency to "oil can" or flutter at high speeds unless they are stiffened with an inner reinforcing member. The hood inner members are adhesively bonded to avoid unsightly weld marks. "Hershey drops" of plastisol adhesive are used in the assembly of hood inner and outer panels. The outer panel is often hem flanged around the periphery of the inner panel to immobilize the parts until they cure in the paint oven. Modern plastisols are able to absorb thin films of oil from the metal as they cure. This ability to bond through oil is of immense value in an industry where thorough cleaning before assembly is traditionally a problem.

These plastisols, while not thermosetting, are able to function as structural adhesives because of the large bond areas and the relatively low loads involved. Furthermore, they endure virtually no peel or cleavage stress, and the tensile loads involved are cyclic rather than static. Thus the problem of cold flow is not significant.

Epoxies are used to bond various car and truck body panels. The adhesive is set up via a four second induction heat cycle. Final cure occurs in the paint oven.

The double shell method of roof construction uses only about half as many metal stampings as the traditional welded assembly and gives a rigid, vibration-free product. The plastisol is effective because it requires minimal surface preparation and because bond line thickness is not critical.

The use of adhesives for bonding brake linings was introduced in 1949. This technique is also used for disk brake pads, clutch facings, and transmission bands. Brake linings use a nitrile-phenolic film adhesive, as shown in Fig. 1. The assembly is cured under heat and pressure. This process, which has produced millions of bonded brake shoes with an outstanding performance record, illustrates the skillful formulation of an adhesive for a specific performance need. Brake linings must withstand impact and high shear stresses at temperatures which can exceed 149°C (300°F). The film adhesive used combines the high heat and shear resistance of phenolics with the excellent impact behavior of nitriles.

**Table 1. Common Automotive Structural Adhesive Applications.**

<i>Use</i>	<i>Resin</i>	<i>Comments</i>
Body and roof reinforcement panels	vinyl plastisol	bonds through oil
Double shell roof	vinyl plastisol	bonds through oil; prevents flutter
Hood inner and outer panels	vinyl plastisol	bonds through oil; prevents flutter
Brake shoes	nitrile-phenolic	resists heat and impact
Clutch and transmission bands	nitrile-phenolic	resists heat and impact
Window sealants	polysulfides, urethanes	best available method
Plastic bumpers	urethanes	improves performance
Disc brake pads	phenolic	heat resistant
FRP body panels (sports car and truck)	urethane, polyester	used over twenty-five years
Radiator tanks	epoxy	replaces solder
Plastic load floors	polyolefin	electromagnetic cure
Hood hem flanges	vinyl plastisol	reduces flutter

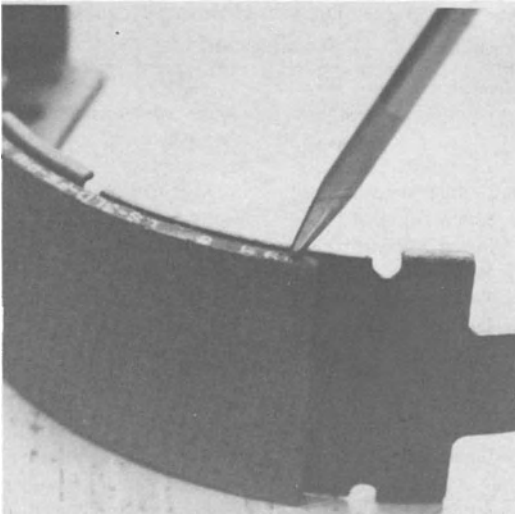


Fig. 1. Adhesive-bonded brake shoes have been used for many years.

Disk brake pads must endure temperatures in excess of  $180^{\circ}\text{C}$  ( $355^{\circ}\text{F}$ ), so the adhesive used is primarily phenolic. It is sprayed on the cleaned shoes and then heated to remove solvent. The adhesive-coated shoe is placed in a die where it contacts the uncured brake pad material. The entire assembly is then heated at  $172^{\circ}\text{C}$  ( $310^{\circ}\text{F}$ ) under 6895 kPa (1000 psi) for 12 minutes to effect the cure.

Epoxies have traditionally been little used by the automotive industry because of their cost and the need for fairly clean surfaces. They are employed only when their durability, strength, or processing ease justifies the additional expense. They have been used to bond roof rail retainers and to form roof-to-quarter panel joints. They are slowly coming into wider use as one-part formulations.

Another automotive application of structural adhesives is that of glass-to-metal assembly. The windshield (front window) and the backlite (rear window) are large, often curved, glass panels which must be secured to the steel body openings. The adhesive used must exclude air, dust, and water and also absorb mechanical vibration which might crack the glass. Ideally the glass-to-metal assembly should contribute to the strength of the body as a unit. Traditionally, these glass panels have either been sealed with butyl rubber tape and mechanically secured or else they have been sealed and held

simultaneously with a crosslinking polysulfide material. The latter technique, of course, results in a more rigid product and is a truly adhesive process.

In recent years, polyurethane adhesives have replaced the polysulfide resins for windshield and backlite installation. The urethane material gives a more rigid assembly which is still able to damp out vibration adequately. The process used to install windshields and backlites actually involves two adhesives. A hot-melt product is used to secure a rubber molding of small cross section (called a dam) to the outside edge of the inner face of the glass. A two-part urethane is then dispensed as a bead on the glass just inside the dam. Next the glass is pressed into place in the body opening, whereupon the urethane deforms and wets the steel surface. The rubber dam prevents the urethane from oozing out onto the exterior body surface. The urethane cures spontaneously and yields a very rigid, leakproof glass-to-metal bond.

Anaerobic retaining compounds are used in a number of structural applications. These include dipstick tube retention and various press-fitted engine block and bearing assemblies.

Two additional structural applications are the use of a two-part urethane in the fabrication of SMC car and truck body parts and the attachment of sun hoof hinges to glass panels. The SMC applications save weight and considerably reduce the time and labor involved in drilling and riveting. Galvanic corrosion and air and water leaks are also reduced.

## HOLDING ADHESIVES

For the purpose of this discussion, holding adhesives are those whose primary function is to attach one material to another without transmitting significant structural loads. A holding adhesive may sometimes be subjected to a fairly heavy load, but the ability to carry this load is not essential to the structural integrity of the automobile. An example of this would be the interior rear view mirror mounting button, which is bonded to the windshield with polyvinyl butyral (Fig. 2). If the mirror is bumped, the bond may need to withstand significant cleavage stress; but the attachment of the mir-

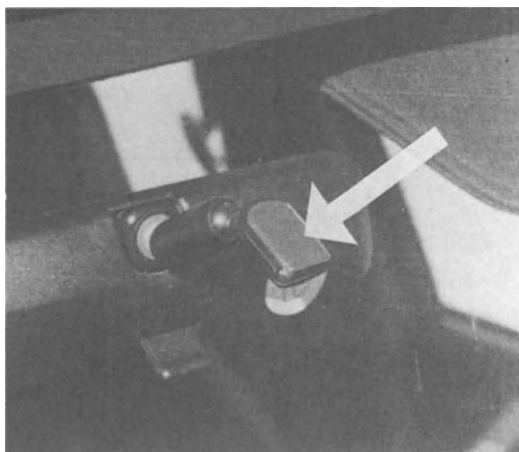


Fig. 2. Interior rear-view mirror holding buttons are bonded to the glass.

ror to the glass is not part of the essential body structure.

Because of their lower strength requirements, holding adhesives often utilize thermoplastic resins. Hot-melt and pressure-sensitive products are particularly popular because of the assembly speeds which are possible.

It is convenient to group holding adhesives as interior or exterior, based on their use inside or outside the passenger compartment. Exterior adhesives in general are subject to more severe environmental exposure and mechanical loading than their interior counterparts.

Typical interior holding adhesive applications are listed in Table 2. One of their major functions is to retain vinyl or ABS films against interior door or sidewall trim panels. The ABS or vinyl sheet material is often vacuum drawn into recesses in the door or trim panel. It may have a tendency to pop loose and creep away from concavities or from the backside of the panels. This behavior, which may be expected whenever the sheet material is under tension, is overcome by the use of adhesives such as epoxies which do not cold flow and which begin to cure when heated in the vacuum forming operation. For panels where there is less tension on the sheet material, hot melts or solvent cements may be used. An example is the use of a hot melt hemming adhesive to secure plastic sheet when it is wrapped over the edge of a door or trim panel.

**Table 2. Typical Holding Adhesive Applications.**

*Interior:*

Trim panel fabric	water base pressure sensitive
Door panel fabric	epoxy spray
Ceiling fabric	solvent cement
Carpet adhesive	polyethylene hot melt
Sound deadener pads	solvent cement
Weatherstripping	solvent cement
Wiring harness clips	vinyl plastisol
Instrument gauge springs	polyamide hot melt
Hem adhesives	polyamide hot melts

*Exterior:*

Body side molding	acrylate pressure sensitive
Wood grain decals	acrylate pressure sensitive
Stripping decals	acrylate pressure sensitive
Weatherstripping	acrylic foam tape
Vinyl roof	pressure sensitives
Mirror-to-metal frame	silicone
Plastic headlamps	two-part urethane
Various locking applications	anaerobics

Solvent cements of the neoprene or SBR type are used in automotive interiors to fasten roof linings, sound deadener pads, and rubber weatherstripping to doors or door openings. Hot melts of the polyamide type are used as carpet-to-floor adhesives and to anchor instrument gauge springs.

Exterior holding adhesives (Table 2) are primarily of the acrylate pressure sensitive or neoprene solvent cement type. They are chosen because of their durability in service, their low temperature flexibility, and their speed and ease of use. Hot melts are used in exterior applications to a lesser extent, particularly in subassemblies such as lamp housings or vinyl roofing seams.

Vinyl roofs (Fig. 3) have traditionally been attached with neoprene solvent cements. Today, the trend is toward pressure sensitive formulations. The fabric is positioned on the roof and pressed downward and outward by hand from the center to remove any wrinkles and air bubbles. Outside edges are generally secured under exterior body moldings. Any seams which exist in the vinyl fabric are usually bonded with a hot melt in a prior manufacturing step.

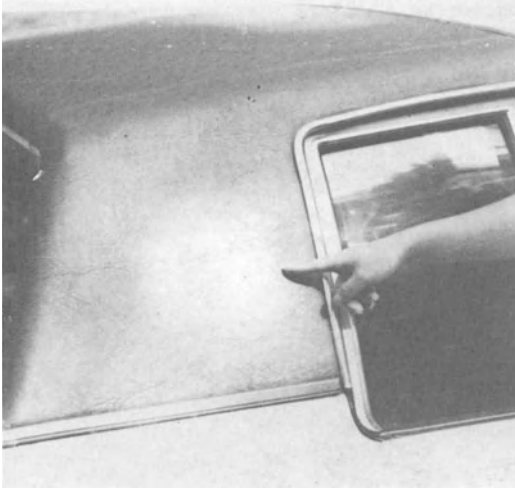


Fig. 3. Vinyl roofs are attached by adhesive.

A second important group of exterior adhesives are those used for attaching trip strips (Fig. 4), and wood grain vinyl sheeting to various body panels. These adhesives are primarily of the acrylate type because of the high tack and good low temperature flexibility of these resins. Fig. 5 shows a door handle insert which is of the same color as the body. This color match is achieved by the use of colored pressure-sensitive tape applied to the recessed portion of the handle.

Miscellaneous script and insignia are generally attached with adhesives (Fig. 6), as are

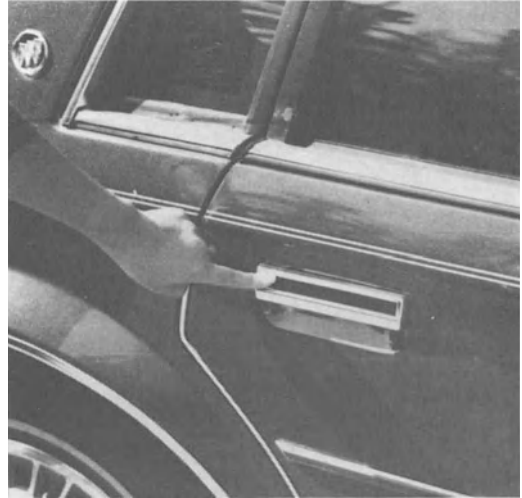


Fig. 5. A bonded body-color door handle insert reduces the need for painting.

decorative stripes. Their use means that stripes like those shown in Fig. 7 can be used without costly paint masking and curing operations. Attachment of insignia and script is significant and challenging from the manufacturing point of view. Considerable savings are possible because separate stocks of parts differing only in the location of mounting holes need no longer be maintained. The entire hole piercing operation can also be eliminated.

Wood grain decals are popular as options on some vehicles. These vinyl materials use an ac-



Fig. 4. Bonded trim strips are widely used in the auto industry.



Fig. 6. Bonded automotive script.



Fig. 7. Adhesive attachment of stripes reduces the need for paint masking.

rylate adhesive and are applied over a thin film of dilute soap solution. The soapy water film permits the vinyl material to be positioned by sliding it around on the surface. The soap and water is then worked out from beneath the vinyl with a squeegee, and adhesion results.

Two additional types of holding adhesives are worthy of mention because their unique properties have made them valuable in the automotive industry. These are silicone adhesives and locking compounds.

A silicone adhesive is used by most, if not all, U.S. manufacturers to attach the exterior rear view mirror to its frame. This is an application where vibration would make mechanical fasteners unsuitable. Low temperature impact and fatigue resistance factors are such that many adhesives would be inadequate. Room temperature vulcanizing silicones, however, have sufficient high temperature flexibility to do an excellent holding job.

Anaerobic locking compounds are unsaturated polyester monomers such as dimethacrylates whose cure (polymerization) is inhibited by atmospheric oxygen. When oxygen is excluded from the bond line, as in the case of threaded fasteners, the resin reacts and the resulting bulk solid locks the parts together.

Figure 8 illustrates a threaded part with a portion of encapsulated locking compound in



Fig. 8. A preapplied threadlocking compound on a threaded part.

position. When the fastener is screwed into place, the compound will be spread out over the thread surface and effective locking will result. Locking compounds are widely used in locations where vibration loosening is a problem. Oil pan screws and door interior hardware fasteners are typical examples. As the demand for more reliable assembly increases, the use of locking compounds, anaerobic or otherwise, will also increase.

### SEALING ADHESIVES (SEALERS AND GASKETS)

These compounds' primary function is to seal out air, dust, or water in order to reduce corrosion or improve comfort. In many cases they may also function as holding adhesives. Their low strength generally precludes their use in structural applications. Typical sealing adhesives are listed in Table 3.

A great many sealer applications are not visible in a modern automobile body. Low viscosity, rubbery sealers are used in virtually all metal-to-metal body joints prior to spot welding. Many of these materials contain gas-forming chemicals which decompose when heated to give a foamy seal which is able to seal out moisture, air, and dirt. They also reduce galvanic corrosion.

**Table 3. Typical Automotive Sealing Adhesives.  
(Sealers and Gaskets)**

<i>Type</i>	<i>Description</i>	<i>Use</i>
Weldable	Low viscosity, may be heat expandable, thermoplastic, stretchy	Between metal to be welded. Inside hem flanges. Seals out water, reduces corrosion.
Hot melt	Polyolefin	Inside box sections which are difficult to reach after assembly.
Body sealers	Bituminous	Seal around fire wall, interior body joints and body drain hole plugs. Prevent air and water leakage.
	PVC	Used under exterior paint where cohesive strength need not be high.
	Epoxy	Use as plastic body solder.
Gaskets	Silicones	As formed-in-place gaskets which can resist heat, cold, and fluids.

Hot melt sealants of the polyethylene type may be used in locations which are difficult to reach after assembly. A stick or rod of the sealant may be placed in a door or rocker panel at a convenient time during the assembly process. When the body is heated in the primer bake oven, the sealant melts and flows by gravity into the joint to be sealed.

A number of other body sealers are extruded over welded joints to keep moisture out and reduce corrosion. Bituminous materials are one example of such sealers. These materials have very low cohesive strength and are generally used in areas which will not be painted. They are used extensively to seal firewall openings, where their ability to adjust to temperature changes without cracking and to reduce moisture are important.

Polyvinyl sealing compounds are used as a replacement for lead body solder for joints which will be subsequently covered by vinyl roofs.

Formed-in-place gaskets are a final example of adhesive sealants. These products reduce the need to stock assorted gaskets and thus enhance assembly efficiency. They are extruded manually or automatically on one of the surfaces involved just prior to assembly. Alternatively, formed-in-place gaskets may be silk screened. Silicones and polyesters are generally the resins of choice because of their adhesion, hot strength, low temperature flexibility, and good resistance to nearly all chemicals.

## THE FUTURE

The years ahead hold considerable promise for automotive adhesives. Currently available products will probably experience a gradual increase in acceptance, particularly in the areas of body structural, hot melt and pressure sensitive holding adhesives. While it is risky to predict the future, it seems reasonable to anticipate additional product development in the following directions:

1. Adhesives which are less dependent on surface cleanliness. Acrylic adhesives which have been used in nonautomotive applications for several years typify this approach.
2. Quicker curing structural products. Structural hot melts may not be too far away. The savings in time, space, and tooling would be significant.
3. The use of acrylic adhesive for metal-to-metal bonding.
4. Lower cure temperatures. Such a development would mean tremendous savings in fuel and fixtures. A new approach to the shelf life-cure temperature dilemma is needed here. Perhaps electromagnetic or friction-induced activation is possible.
5. The real possibility of totally bonded metal or plastic body components, perhaps starting with doors or decklids in order to take advantage of the stiffening properties of adhesives.

# Meter, Mix and Dispensing Equipment: Basic Designs

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Many formulations of reactive adhesives require mixing of the resin and hardener in a critical ratio. This chapter deals with the basic designs of equipment for this purpose.

The most popular meter, mix and dispensing machines have been designed around *gear pumps* and *pistons*, or a combination of both. This chapter will explain how both systems function, their strengths and weaknesses.

In order to select a machine, several questions must be answered:

1. What material is to be dispensed: epoxy, polyurethane, silicone, etc.?
2. What are the characteristics of that material which will affect metering: viscosity (rheology), component ratio, filled or unfilled, abrasive or nonabrasive, pot life?
3. Application, production rate, volume required, continuous or intermittent dispensing?

## THE GEAR PUMP SYSTEM

The circuit diagram in Fig. 1 shows the common gear pump metering system. The degree of sophistication governing the driving and monitoring of these devices varies from manufacturer to manufacturer, as does the cost.

In Fig. 1, the letters A and B represent the supply tanks. Tank A is usually the resin sup-

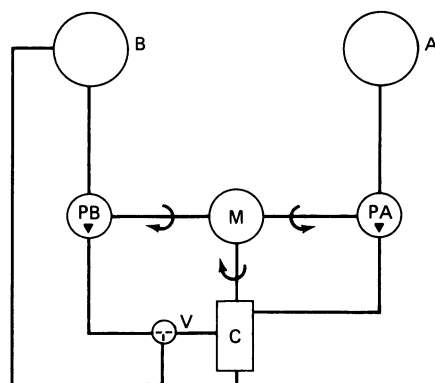


Fig. 1. Gear pump metering circuit. PA—resin metering pump; PB—hardener metering pump; V—three-way valve; M—drive motor; C—mixer. A—resin tank, B—Hardener tank.

ply and Tank B the hardener supply. These tanks can vary in size from one quart up to 55 gallons. They may be ASME tanks which are capable of handling pressures to 75–80 psi. The tanks may be heated or cooled and may incorporate agitators, driven by electric or air motors.

The tanks may be equipped with liquid level controls which sense the amount of material in a tank. These sensors will send a signal, causing a pumping device to start filling the tank. Upon reaching a predetermined liquid level, a sensor will signal the filling device to stop. A system such as this makes the machine com-



pletely self-sufficient so long as the main material supply is maintained.

The letters PA and PB represent the metering pumps. These pumps are fixed displacement type, using either gears, diaphragm, or piston to displace the material being pumped. Only gear pumps and piston pumps will be covered, as diaphragm pumps are not popular.

Gear pumps vary in the precision with which they pump material against a resistance. The machine designer selects a specific pump according to the characteristics of the material being processed and the production requirements. Materials having viscosities, 500 cps and up, do not require the precision of pumps that pump materials with viscosities in the 50–500 cps range. Pump speeds (rpm) must be such that pump cavitation will not occur.

Gear pumps are very accurate metering devices and when used properly can do an excellent job. They cannot, however, be used with materials containing abrasive fillers, or highly filled materials which will prevent lubrication of moving parts. The filler material will cake up in the pump, causing the pump to jam. On the other hand, materials which have relatively high viscosity, but are still pumpable, cause the pump to run at near 100% efficiency since slip is at a minimum.

The advantage of the gear pump system (Fig. 1) is its simplicity. The system contains no check valves. It may contain a three way valve (V) to divert hardener from the mixer to the tank for the purpose of ratio checking or purging the mixer with resin.

The letter M denotes the drive of the pumps. This could be a simple gear head motor linked to the pumps via gears or chain and sprocket. It could also use a SERVO motor drive system. With this setup, ratio may be changed at will. With gears or sprockets, these must be physically changed in order to effect a change in ratio.

The letter C denotes the mixer of the machine. The two most popular types are the *dynamic* and the *motionless* mixer.

### The Dynamic Mixer

This mixer is simply a rotating (usually bladed) agitator within a chamber. The space between

the tip of the blades and the inside diameter of the mixing chamber is very small. Usually, part A (resin) will enter the chamber behind the part B (hardener) entry port. In some cases, a check valve is used to prevent the intrusion of resin into the B side of the machine as the result of a drop in B side system pressure. If this occurs, the valve closes, preventing part A from entering.

The mixer is driven by either electric or air motor; mixer speeds vary from 1700 up to 20,000 rpm.

Mixer shaft seals range from V-ring packings to mechanical rotary seals. The degree of back pressure and speed a mixer can tolerate is a function of mixer shaft seal type.

V-ring packings would require lubrication to extend the life of the seal, especially at high speeds and pressures. Mechanical (rotary) seals do not require lubrication, but have speed and pressure limitations, red lined by the manufacturer of the seal. Maximum speed for seals in the 0.500–0.625 in. shaft diameter range is about 4500 rpm at 100 psig system pressure.

The dynamic mixer can mix a variety of formulations since mixer speed, size, and resident time (the time the mixture spends in the mixing chamber) can be varied.

The disadvantages are that it does require maintenance, primarily cleaning and seal replacement. It cannot take high back pressure without premature shaft seal failure. In addition, being a mechanical device, it takes energy to drive; seals create frictional heat in addition to the heat generated by the shear action of the blades through the mixture. Mixing temperatures can exceed 120°F but this depends upon the rate of the material through the mixer and the temperature of the components being mixed. It should be noted that the gel time of the material being processed is no longer the published time and in all probability will be shorter due to the heat generated by the mixer. A good rule of thumb is: for every 10°C rise in temperature the pot life is reduced by one-half.

### The Motionless Mixer

This mixer does not require mechanical energy to achieve the mixing of the two streams. Mix-

ing is accomplished by geometric shapes presented to the stream of material. The motionless mixer has no moving parts, and with the advent of the inexpensive throwaway mixer and mixers which can be disassembled and cleaned, it must be considered as a mixing alternative in the design of a machine.

The motionless mixer, unlike the dynamic mixer, cannot be relied upon to mix any and all formulations. Mixing is aided by increasing the back pressure by restricting the flow at the exit end of the mixer or increasing the throughput (the speed at which the materials pass through the mixer). The next step to obtain a good mix would be to add another mixing element which will increase back pressure. What must be realized is that a motionless mixer may do an excellent job mixing one formulation, but may fail to mix another.

The factors which influence the success or failure of a motionless mixer are: material viscosity (rheology), ratio, flow rate, and compatibility of the materials. If resin (A) and hardener (B) have widely differing viscosities, e.g., 50,000 cps (A) and 50 cps (B), the material having the lower viscosity may just "rat-hole" through the mixer, resulting in a poor mix. If a formulation calls for a ratio range of 3-5 parts per hundred, it may be difficult to mix.

The mixer also creates a great deal of back pressure (depending upon viscosity), approximately 5-10 times the pressure created by a dynamic mixer. In addition, the passageways slowly close (due to the curing of the stagnant layer of material), restricting the flow, which subtly places added burden on the pumping device of the machine in the form of back pressure.

At this point it must be apparent that the material intended for use should be selected with care that it be machine compatible. The supplier should be able to confirm this. If possible, one should insist on nonabrasive fillers or no fillers at all, and reasonable, easy-to-obtain ratios. If possible, ratios such as 1-2 parts per hundred should be avoided, as they are very difficult to hold without constant attention to the metering equipment and the condition of the materials being processed. One should insist on color changes when mixing resin and hardener;

this aids in verifying proper mixing and adequate purge of the mixing chamber.

In conclusion, both mixer types are excellent tools if used with suitable formulations.

## THE METERING CYLINDER SYSTEM

The basic circuit diagram for this type of metering system is shown in Fig. 2. The resin (A) and hardener (B) tanks can incorporate the same features as described previously for the gear pump metering system, in addition to mixing methods.

The valves identified as E and F are called *charge valves*. The function of these valves is to prevent any back flow of material to tank when the metering pistons (cylinders) PA and PB move forward to dispense material through the discharge valves.

Valves C and D are called *discharge valves*. Their function is to prevent any suckback of material into the metering cylinders, which could occur during the charging cycle.

The letters PB and PA denote the *metering pistons*. These could be pistons with V-ring seals as shown in Fig. 3(a), cup type piston [Fig. 3(b)], or blind rod cylinders [Fig. 3(c)].

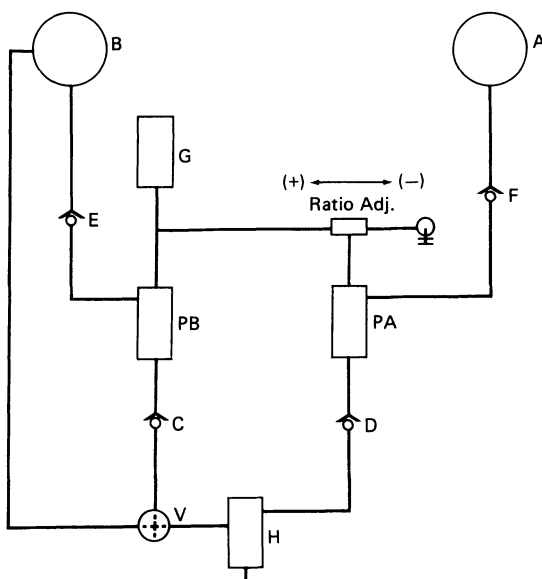


Fig. 2. Single-acting metering system. A, B—material tanks; C, D—discharge check valves; E, F—charge check valves; G—drive cylinder; H—mixer; PA—resin cylinder; PB—hardener cylinder; V—hardener bypass valve.

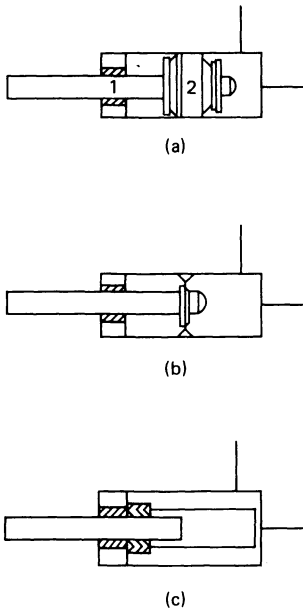


Fig. 3. Piston seals. (a) Chevron V-ring seal; (b) piston cup-type seal; (c) blind rod (no piston) cylinder.

The designs shown in Figs. 3(a) and 3(b) are useful when nonabrasive materials are being used, although some degree of success has been achieved with abrasive materials using polyurethane seals in conjunction with a hard chrome plated cylinder wall. The cylinders in Figs. 3(a) and 3(b) each incorporate a tank which supplies the bearing side of the cylinder with lubrication in addition to excluding air from the metering cylinders. This is essential when moisture-sensitive materials such as isocyanates or polyurethanes are used. The lubricant is usually an inert plasticizer.

From a design standpoint, Fig. 3A is superior since it contains a piston assembly which is supported at two points (1 and 2). This piston rod assembly is capable of taking more side load than the cylinders shown in Fig. 3(b) or 3(c). The cylinder shown in Fig. 3(c) is a blind rod cylinder, and when equipped with the proper shaft scrapers and seals will do a good job with *abrasive materials*.

The check valves, C, D, E, and F, are the heart of the system. If they foul up, the best metering pistons or mixer cannot remedy an off-ratio condition. These valves range in complexity and cost from a simple spring-loaded check to expensive powered valves of either

spool, poppet or rotary designs. The selection of a valve type is based upon the material being processed.

### Spring-Loaded Check Valve.

This valve (Fig. 4) is relatively inexpensive and will perform well with low viscosity liquids. It is used extensively in oil and pneumatic circuits, but has some limitations when used to control very viscous materials. It can momentarily open when subjected to abrupt pressure changes.

Spring-loaded valves appear to be great strainers, especially on low ratio systems, where the fluid flow velocity is low. In this case, the valve would only crack open, presenting a very small opening through which the liquid flows, as a result, any contaminants could be trapped between the ball and seat. In some cases, crystals formed by moisture can cause valve problems.

When operating from pressurized material tanks or from transfer pumps, the closing spring pressure required for the discharge check valves must be greater than the highest pressure developed by the transfer pump during the charging cycle. Otherwise it is possible to open the discharge check, allowing unmetered material to enter the mixing chamber. This can easily be checked by observing if a steady drip of material is present at the dispensing nozzle.

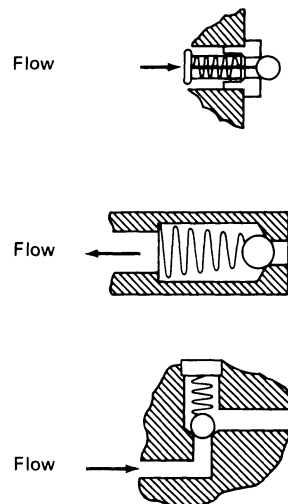


Fig. 4. Check valve arrangements.

### Powered Check Valves.

These valves are usually driven by a solenoid, a pneumatic cylinder, or a mechanical linkage. If properly designed, they will not function as displacement devices and will be held closed by system pressure.

The seats of these valves are usually soft, made of plastic such as Teflon, polyethylene, or nylon. The valves tend to form their own seat configuration when cycled several times.

The weak point in this valve is the actuating shaft, which contains a seal. This shaft connects the poppet spool with the actuator. If this seal fails, no matter how good the internal seals, the valve must be repaired.

In terms of cost, the powered check valve is more expensive than the spring loaded ball check valve, not only because of design differences but also because of the control devices required for operation. Regardless of the powered valve's cost, it is a comfort to know that the valve is going to operate regardless of the material or operating conditions.

Powered valves, being operated by one of several types of actuators (solenoids, air cylinders, and rotary actuators), lend themselves well to microprocessor-controlled machines.

The machine described in Fig. 2 may be classified as a single-acting metering device. This device requires time to recharge, once cylinders PA and PB have discharged. If the materials are low in viscosity, this time may be as short as 2–5 seconds. If viscosities are high, the recharge time can be 15–30 seconds or longer.

An important factor: in many applications, tanks A (resin) and B (hardener) must be pressurized to achieve meter cylinder recharge within a reasonable time period. In addition, heating of the materials will reduce recharge time. If the proper recharge of the cylinders is not achieved, an off-ratio condition will exist.

The circuit diagram in Fig. 5 shows a double-acting metering system. The principles of operation are the same as those used in Fig. 2. In this device, the machine is driven by transfer pumps A and B which charge (fill) the metering cylinders with material. The charge and discharge valves allow the metering cylinders to be filled with material during the dispensing cycle. No recharge time is required. An explanation as to how this system works follows, using Fig. 5 as a guide.

At a given signal, transfer pumps A and B will start pumping. At that same instant *all*

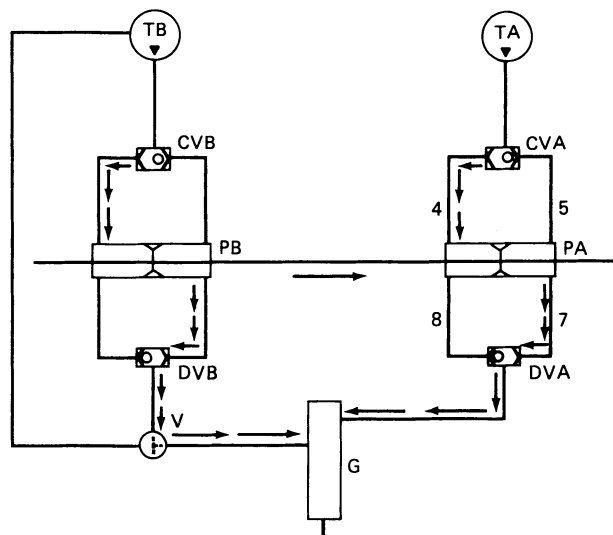


Fig. 5. Double-acting cylinder-type metering system. CVA, CVB—charge (suction) valves; DVA, DVB—discharge valves; PA, PB—metering cylinders; V—hardener bypass; TA—resin transfer pump; TB—hardener transfer pump; G—mixer.

charge and discharge valves will shift to the position indicated. On the resin side, valve CVA has isolated line 5, allowing pressurized material to flow through line 4 to metering cylinder PA. Cylinder PA moves, pushing material through valve DVA which isolated line 8, allowing material to flow through line 7 to mixer G. The sequence is the same for the hardener (B) side, and both sides act simultaneously. Cylinders PA and PB, upon reaching the end of their stroke (length of travel), actuate a limit switch which signals all charge and discharge valves to switch, reversing the flow of the material and the travel direction of cylinders PA and PB.

In Figs. 2 and 5 the discharge checks are shown individually, but in actuality all the check valves may be combined into one or two single units, depending upon the metering system. In other designs the charge check may be the piston itself (Fig. 6). As the piston in Fig. 6 is driven forward, material is pushed back to tank until the metering stage is started. That happens when the leading edge of the piston seal passes the tank port and makes contact with the cylinder walls. Visualize two such devices hooked to a single drive; this produces a relatively simple two-component metering device. Some cautions: The entry of both resin (A) and hardener (B) pistons into the metering stage must be exact; any lead or lag between pistons constitutes an off-ratio condition (how much off ratio depends upon the lead or lag). On the recharge, the piston is being pulled back, result-

ing in a vacuum within the metering chamber. If strong enough, this vacuum will collapse the piston seal and allow material to enter the chamber. This is of no concern so long as the piston seal recovers to seal during the metering cycle, as the piston pulls out of the metering zone, if the recharge is not controlled, the sudden surge of material caused by the vacuum break can momentarily open the discharge check, allowing unmetered material to enter the mixing chamber. The rod check valve shown in Fig. 6 helps eliminate this problem.

## RECOMMENDED ACCESSORIES

### Positive Cutoff

This device is usually located at the dispense nozzle. Its function is to prevent dripping. It is used where precise shot sizes are required without tailings.

The positive cutoff must be timed with the cycle of the machine. It must open at the instant the dispense button is depressed and is set to close a few milliseconds after the dispense button is released. The designs range from a simple scissor arrangement to the manipulation of valves: pinch valves, collapsible tubes and duck bill valves. The best are those which operate without contacting the mixed materials.

### Pot-Life Guard

This device prevents the accidental curing of mixed material in the mixing chamber. The de-

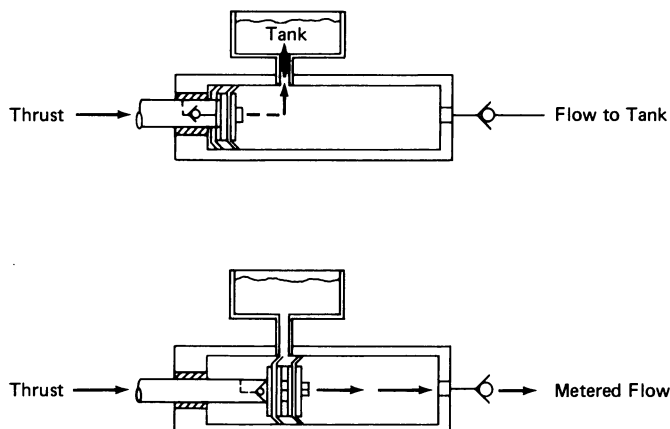


Fig. 6. Piston charge check.

**Table 1. Meter, Mix and Dispensing Equipment.**

Accumetrics Box 843 Elizabethtown, Kentucky	Hardman Industries, Inc. 600 Cortlandt Street Belleville, New Jersey 07109
Amplan, Inc. 200 Egel Avenue Middlesex, New Jersey 08846	Liquid Controls 7576 Freedom Avenue N.W. Box 2747 North Canton, Ohio
APC INC. 1123 Morris Avenue Union, New Jersey 07083	Maguire Products, Inc. 6 Miller Road Edgemont, Pennsylvania 19028
Ashby Cross Company, Inc. 20 Riverside Avenue Danvers, Massachusetts 01923	Otto Engineering Corp. 2 Main Street Carpenterville, Illinois 60110
Fluidyne Instrumentation 2930 Lakeshore Avenue Oakland, California	Pyles Industries, Inc. 28990 Wixom Road Wixom, Michigan 48096
Glenmarc Manufacturing, Inc. 300 South Harbor Suite 600 Anaheim, California 92805 or 330 Melvin Drive Northbrook, Illinois 60062	Resi-Mix 26 Ashmont Avenue Whitinsville, Massachusetts 07588
	Sealant Equipment & Engineering Co. 2100 Hubbell Oak Park, Michigan 48237
<i>Spray Equipment</i>	
Binks Manufacturing Company Franklin Park, Illinois	Zicon Mt. Vernon, New York

vice is simply a flip-flop timer circuit. The first timer monitors the off time (the time from the end of the dispense cycle to the preset time programmed into the first timer). This time is based upon the pot life (gel time) of the mixture. When this timer times out, it starts the second timer going. At this time the dispenser starts. This continues until the timer runs out, at which time dispensing stops. This is called *purge time*, and is a function of mixer volume.

In conclusion, the methods of dispensing reactive materials are varied. We are seeing the meter, mix, and dispense machine being integrated into computer controlled production lines. Dispensers are working successfully with

two- and three-axis indexing tables and robots having both point-to-point and continuous-path capabilities.

With the increased use of adhesives in the construction of structural assemblies, the need for dispensing equipment should expand. Indeed, control of the machines will become more complex as they find their way into the world of robotics and automation.

## EQUIPMENT SUPPLIERS

Table 1 shows suppliers of equipment for metering, mixing and dispensing, as well as spray equipment.

# Robotic Dispensing of Sealants and Adhesives

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## INTRODUCTION

The dispensing of adhesives and sealants (hot, warm, or cold) has been established as a proven market for the application of robotics. Robots are being used across industries for applying adhesive and sealants to increase quality and to reduce labor and material costs. The automotive segment has led the way for the application of robotics. This chapter will deal with that segment and some of the criteria associated with automating particular applications, emphasizing the relationships between the application objectives and the adhesive/sealant dispensing equipment. Successful applications take into consideration the capabilities and limitations of the adhesive/sealant materials, the dispensing equipment, the tooling and fixtures and the robot.

Selection of the robot and the dispensing equipment are of primary importance when automating sealant and adhesive application processes. Those installations that have taken into account all aspects of the application requirements have been successful.

Robots are used to dispense adhesives and sealants throughout the automotive industry today. Automation requirements will be examined for windshield bonding to the vehicle, door manufacturing, passenger compartment interior seam sealing, and the application of sealants during the buildup of the vehicle body. These account for the vast majority of robotic sealant and adhesive dispensing applications in the automotive industry.

## DISPENSING EQUIPMENT FOR ROBOTIC APPLICATIONS

The three elements of a dispensing system are the pumping system, the delivery or header system and the dispensing gun or valve. Careful selection of each element is required to deliver the desired bead at the required flow rate. Lack of performance in any one of the three elements will limit the benefits of the automated dispense system.

### Pumping System

The pumping system is typically made up of two bulk unloaders, two feed hoses delivering the pumped material to a common changeover manifold and a system controller. Two bulk unloaders (A and B) are normally selected in a

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Text excerpted from "Robotic Dispensing of Cold Sealants and Adhesives—New Advancements," presented at the 1987 Fall Seminar of The Adhesive and Sealant Council, Inc.

robotic system to provide a continuous flow of material. The bulk unloaders could be provided with either piston or gear pumps, depending on application and material requirements.

A heated dispensing system is used here for illustration, however, many of the system variables are equally relevant for cold dispense systems. In a typical heated sealer application (Fig. 1), bulk unloader A would be the on-line unloader. The on-line unloader is the unit currently heating the material to application temperature and pumping the material to the changeover manifold at the required temperature, pressure, and flow. Bulk unloader B is the standby unloader and will usually be at a setback (reduced) temperature to minimize the amount of time the sealer is at application temperature while ensuring that minimum time is allotted to come up to full application temperature when commanded from the system controller.

The control logic for the two bulk unloaders is as follows:

- Bulk unloader A provides material as needed by the dispensing guns while bulk unloader B waits in a standby (reduced temperature) mode until needed.
- When bulk unloader A reaches a predetermined level known as *Low drum*, a limit switch sends a signal to the system controller, which in turn increases the set-point temperature of bulk unloader B from the setback temperature to the required application temperature (usually the same as A).
- When bulk unloader A reaches *empty drum*, another limit switch sends a signal to the system controller indicating that bulk unloader A is out of material. The system controller automatically then switches bulk unloader B to *on-line* status and signals manufacturing personnel that a changeover has occurred and that a new drum of material is required. Bulk unloader A will remain at application temperature to facilitate easy removal of the drum follower plate. After the follower plate has been raised and the empty drum removed and replaced by a new drum, the follower plate is then reinserted followed by purging of air from beneath the fol-

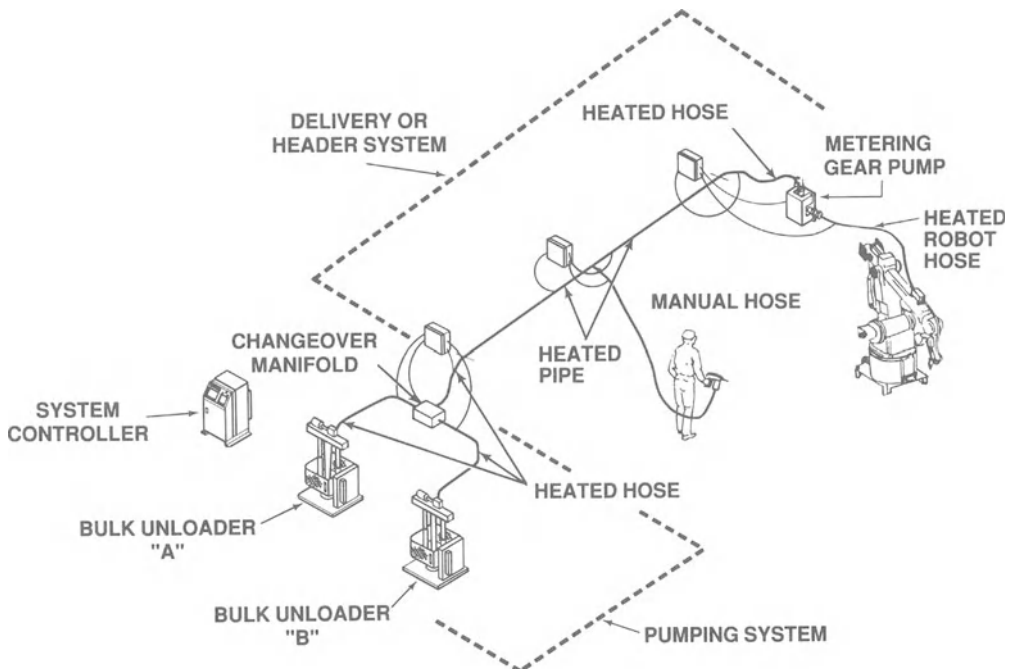


Fig. 1. Typical dispensing system configuration with robotic and manual application points.



lower plate (total time takes about 3–8 minutes depending on training and skill). A *ready* button on unloader A is then activated by the operator to place drum A into the standby mode by the system controller.

Bulk unloaders come in three common sizes: 5, 55, and 300 gallons. Selection of the appropriate size is application dependent and requires several considerations. First, acceptable time intervals between drum changes should be determined. The volume of the bead deposition per application and the number of applications per hour will dictate the amount of time between drum changes. Some materials have a very long shelf life and therefore provide more flexibility in container size. Other considerations are economies of larger drums and accepted plant practice for material handling. For materials having shorter shelf life or where there is low daily material usage, a smaller drum size is optimal. For example, in the process of building vehicle doors, approximately 2.1 cubic inches of material are required in the assembly process. If 120 doors per hour are manufactured to meet production requirements, then 252 cubic inches (1.09 gallons) per hour will be needed from the pumping system. In this case the proper bulk unloader/material container size would be 55 gallons and not 5 or 300 gallons. A 55 gallon drum of material allows for 6.3 days per bulk unloader of production, as compared to 4.6 hours for a 5 gallon drum or 34.4 days for a 300 gallon container. Sized correctly and with tandem bulk unloaders, scheduled drum changes can be made instead of emergency/reactionary drum changes. The tandem unloaders also provide backup for each other in the event of failure, or during system maintenance, and they output a continuous bead even during the automatic changeover sequence.

System design and controls monitor material usage and other system conditions to ensure continuous production. Another feature of a well designed automatic control system is diagnostics, particularly in the area of pinpointing the location of failed heaters or temperature sensors. A system that monitors all temperature fluctuations throughout the distribution path,

providing immediate feedback, has advantages relative to inferred sensing controls. An example of inferred sensing would be a controller that was designed to monitor the minimum setpoint temperature. For inferred sensing, an alarm will sound when the actual running temperature reaches the minimum setpoint temperature. Due to the inferred temperature sensing mechanism a time delay of 20 minutes may elapse before a system failure is detected. A control system that pinpoints heater loss and location within the system immediately prevents lost production and simplifies system troubleshooting. Immediate feedback also signals maintenance before critical downtime occurs.

Another system control feature often required for robotic systems is an automation interface card that allows signals to be sent back and forth between the robot, the cell controller, and the system controller. Signals such as SYSTEM READY indicate that there are no major malfunctions and that the system has reached application temperature. Another valuable system control feature in a robotic dispense system is simplified gun purge capability. In the event that skilled personnel that know how to facilitate a purge signal from the robot cannot be located, an easily located button on the system controller for this purpose is important. All of these features are needed to minimize downtime, which is often the yardstick by which robotic systems are measured.

### Header System

The delivery or header system usually consists of flexible hoses and rigid pipes. The design of this system must be coordinated with the plant layout, the material to be dispensed, and the instantaneous material delivery rate required. The two primary factors are material and delivery rate. Each material to be dispensed (adhesive or sealant) requires a unique and specific pumping pressure based on header size (hose and pipe inner diameter) and delivery rate. Calculations should be made to estimate system pressure drop for a proposed system configuration to determine if sufficient system pressure availability exists. Tests should also be conducted to verify system design. These calculations and tests should take into account

maximum robot velocity and bead size to be dispensed to determine instantaneous delivery rate. Available cycle time is *not sufficient* information for calculating instantaneous delivery rate requirements. Available dispense time and maximum robot velocity are also critical considerations for proper selection of delivery system components.

Other considerations for both heated and unheated delivery/header systems include modularity for system configuration or redesign, backup temperature sensors, hose and pipe sizing, ease of maintenance, and routing of hoses on the robot with regard to its movements during robot cycles and for robot maintenance.

### Dispensing Gun

Over the years many attempts have been made at designing a robotic dispensing valve. The progression from each design has been evolutionary rather than revolutionary in the attempt to design dispensing equipment that has the same level of performance as the robot. Many of the dispense valve designs have fallen short of meeting the same performance criteria that robots have met in the area of speed of response. Recently Nordson Corporation released a variable orifice dispensing gun known as the Pro-Flo™ System (patent pending) that has met the design criteria that all systems have tried to obtain—speed of response equal to or greater than the robot. The Nordson Pro-Flo™ System (Fig. 2) has the ability to adjust material flow rate as the robot adjusts velocity to achieve uniform bead deposition.

Bead control, or management of bead deposition, is driven by both the manufacturing process and the rheology of the materials to be dispensed. Process requirements may dictate a short cycle time to dispense the material, hence varying velocities and accelerations are required to meet path accuracy and cycle time constraints. As the robot varies its velocity to meet these sometimes opposing constraints, management of the deposition becomes more important in dispensing uniform beads. As materials develop, the amount dispensed, as well as the cost, play an important role in the dispensing equipment selection. A material dispensed in too small or large a quantity may

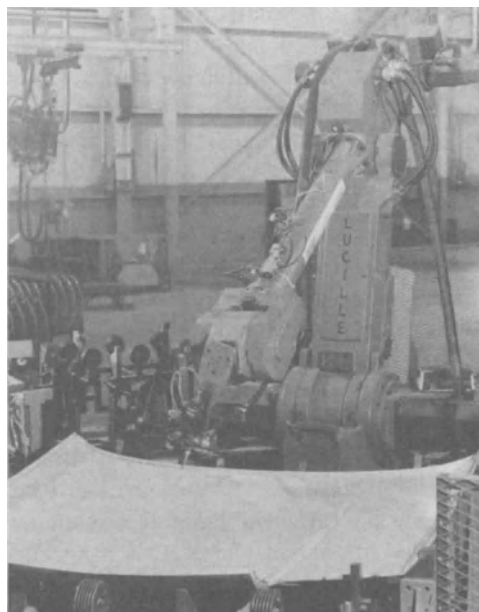


Fig. 2. Robotic application of hem flange adhesive at BOC-Lansing's Reatta Craft Centre featuring a Nordson® Pro-Flo™ System.

negatively impact part quality as well as material usage.

The key to uniform material deposition using robotics is the interface between the equipment and robot. The robot sends and receives electrical signals from the dispensing gun in a continual feedback system. The signals sent from the robot to the dispensing system cover basic functions, such as gun on/off, while the dispensing system offers diagnostic signals that indicate fault conditions and provide troubleshooting assistance. These signals are important because they aid in minimizing manpower for checking quality (i.e., verifying bead deposition), system maintenance and downtime.

### Typical Methods of Bead Management

Alternative methods of bead management include the pump and gun combination, the shot metering system, and the electropneumatic control of gun orifice size relative to changing robot velocity and to hydraulic and pneumatic pressure variations. The relative merits of each method will be discussed.

The simplest method for robotic dispensing is the pump and gun combination. The pump is

used to unload material from bulk containers and create hydraulic pressure in a distribution system. The gun is used to turn the flow on and off while at the same time providing a fixed flow resistance to the material. The greater the flow resistance, and consequent pressure drop, the greater pump pressure required to increase flow or bead size. There are many drawbacks in this type of system. Variations in pump pressure output during the robot cycle result in variations in flow (bead size) which can result in bead deposition which does not meet process specification. Variations in robot velocity combined with no bead control other than gun on/off can also result in inconsistent bead size. As a result of changes in robot velocity, excess material is often applied to ensure that the minimum bead size is always applied.

Simple pump and gun dispensing equipment of this type requires constant robot velocity to provide a constant and consistent bead. However, to achieve the objectives for cycle times, productivity goals, and quality needed to meet today's standards, robot velocities are varied to maintain path accuracy, especially in cornering. The equipment configurations and limitations discussed are often frustrating to the manufacturing/process engineer who is responsible for product quality and productivity.

Programmable transfer pumps, better known as shot pumps, are another equipment variation available for robotic dispensing of adhesives and sealants (Fig. 3). In shot pump systems, the dispensing gun has a fixed needle-and-seat arrangement, providing a constant orifice diameter.

The shot pump may be air, hydraulic, or electrically controlled. The shot pump controller accomplishes bead management by processing an output control signal from the robot and varying the shot pump output proportional to the robot signal. This robot output control signal is either a constant DC voltage or a variable DC voltage that is proportional to robot tool center point (TCP) velocity. This technique provides greater control over the preceding method of constant pressure and fixed orifice. However, there are several constraints affecting the application of shot pump dispense systems.

The first constraint is floor space requirements for the shot pump and shot pump controller. The second constraint is the distance between the shot pump and the gun tip. Typically, the shot pump is one hose length away from the dispensing gun tip, causing response delays in the required fluid output variance. To compensate for the delayed change in material flow at the gun tip, robot manufacturers have tried both prepressurizing the system and programming the robot in anticipation of material output. The resulting system hysteresis from pressurizing and uncontrolled pressure decay often provides poor overall bead management.

As mentioned earlier, it is possible to model the dispensing systems performance characteristics and to compensate for them in robot programming. However, due to the complexity of the dispensing configuration, overall bead management is typically not optimized. Reported system response time to changes in the robot signal varies from 200 milliseconds to

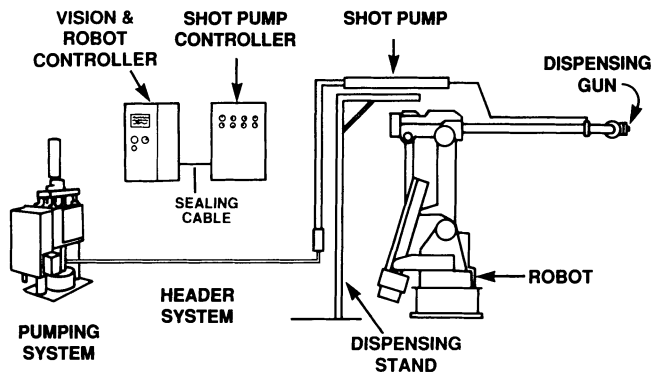


Fig. 3. Typical system configuration for a shot meter installation.

over 1 second. Today's robots are known to update and respond in as little as 30 milliseconds. With a robot velocity of 20 inches per second a 200 millisecond response would result in an incorrect bead size for up to four inches while the metered output lags behind the robot signal.

The remaining two issues associated with shot pumps, limited dispense output volume and a condition known as "packing out," pertain directly to the pump itself. These two issues are interrelated. A properly sized shot pump will evacuate all material in the cylinder during the dispense cycle. As a result, the system is inflexible to meet increases in dispensing requirements. Between the time the dispensing equipment was first specified and the actual installation date, the material dispensing requirements are likely to have changed due to automobile design changes or to meet the manufacturing/tooling capabilities. If the shot cylinder is oversized relative to the specification, then a given amount of material will not be evacuated for each application. The material remaining in the cylinder is then subjected to repeated high pressure applications, potentially causing fillers to be compacted due to squeeze-out of the carrier (e.g., plastisol). This compacting, also known as packing out, results in a solid plug in the cylinder that cycles back and forth for each application. Problems occur when bits and pieces of this solid plug break off and cause nozzle clogs during dispense. Once a nozzle clog occurs, the shot pump will usually continue to pressurize the system until the weakest system component ruptures to relieve the overpressure condition.

Another variation of the programmable transfer pump involves the use of an electric servomotor-driven gear pump. These pumps have the same deficiencies associated with shot pumps. Response lags caused by gear pump inertia as well as the distance between the pump and the dispensing gun contribute to limited control and poor response over the length of the bead. In addition, floor space is consumed by the control panel required for receiving signals from the robot and sending control signals to the servomotor controller and ensuing servomotor/gear pump combination.

Pump wear is another problem associated

with gear metering systems since tolerances must be held tight to minimize pump leakage across the side plates from high upstream pressure. In addition, many of the materials dispensed have a high content of abrasive fillers, further contributing to excessive pump wear.

## ADVANCEMENTS IN DISPENSING TECHNOLOGY

To meet the challenge of today's robotic applications, a new approach to automated dispensing has been developed involving electro-pneumatic control of the gun orifice size as a function of robot velocity. The system is able to respond with equal or greater speed than the robot-to-input command signals. The system is also designed to handle a wide range of materials and features a linear relationship between robot input command voltage and flow (Fig. 4) for accurate bead proportioning. Additional product features include near-zero floor space, ease of maintenance, repairability, and modular components for compatibility of parts across many models of guns. Finally, the gun design incorporates dowel pins and piloted fits to ensure accuracy and repeatability from gun to gun for successful automation.

For accurate metering and flow adjustment, and to ensure fast response time, adjustment of flow occurs close to the gun nozzle. To accomplish this, pressurized material flows into the gun and across a variable orifice. The variable orifice is comprised of a solid carbide needle and seat for maximum wear resistance. Downstream of the needle and seat, but before the nozzle, a pressure transducer provides pressure

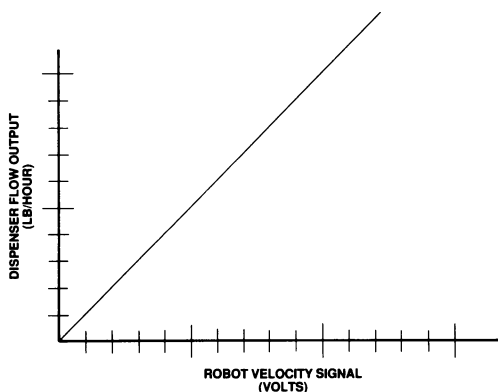


Fig. 4.

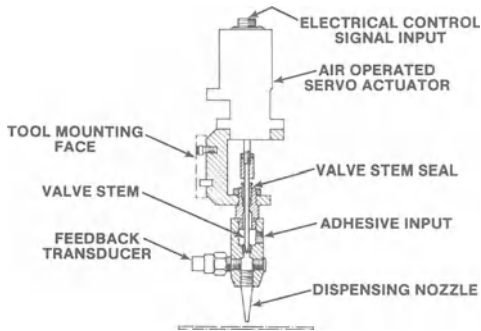


Fig. 5. Variable orifice dispensing gun. (Courtesy Nordson Corporation, Amherst, Ohio.)

feedback to the dispenser's closed loop control (Fig. 5). A nozzle pressure control is used to compensate for variations in both hydraulic and pneumatic system pressures.

Figure 6 is a graphical presentation of the control loop illustrating the operating sequence. The diagram shows the relationship between the robot signal, pneumatic servo, hydraulic/pneumatic pressure supplies, pressure feedback, and nozzle orifice. As the diagram illustrates, a change in the incoming robot signal causes a change in the controlled nozzle pressure and subsequently adjusts gun orifice size to provide accurately controlled material flow.

Four operator-adjustable controls are used to ensure ease of use and maximum controllabil-

ity. The first control is a purge function. With a simple switch closure from the robot, the system is placed into a purge mode that is fully controllable via the system control settings. Increasing the purge value causes an increase in the flow, while decreasing the purge setting decreases the flow. During the purge cycle the robot controls the duration of gun on time by a timed switch closure. The second control setting controls bead size during the dispense cycle. The bead size control function and incoming robot signal are multiplied together to form a proportional control. To ensure the linear relationship between input signal and flow, two additional controls are used. The two additional controls, referred to as *high speed* and *low speed*, compensate for material properties such as shear thinning. These controls transform material nonlinearities into a linear function over a wide range of flow.

Figures 7 and 8 display the speed of response by the system during the course of the sample path. The path (Fig. 7) has speed variations ranging from 4 in./sec to 16 in./sec. The inverted pressure transducer signal and the accompanying robot command signal are illustrated in the response curve in Fig. 8, which also shows how the system compensates for pump wink. Pump wink occurs when the piston changes direction and causes a dip in the system supply pressure. Variations in pump

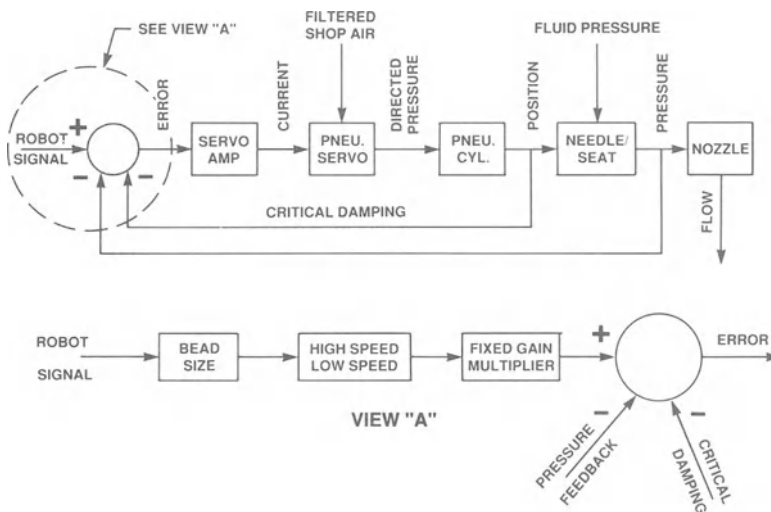


Fig. 6. Analog control loop for variable orifice dispensing gun. (Courtesy Nordson Corporation, Amherst, Ohio.)

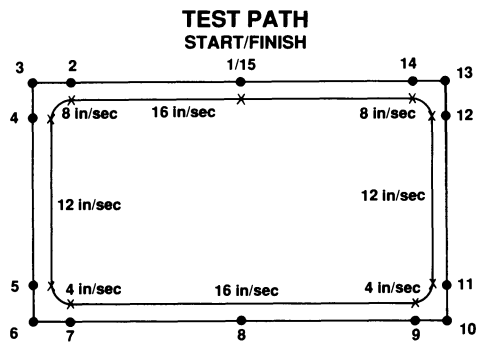


Fig. 7. Test path with varying velocities. (Courtesy Nordson Corporation, Amherst, Ohio.)

supply pressure such as pump wink are minimized by the electropneumatically controlled dispense gun to provide uniform material flow.

### APPLICATIONS

Dispensing of adhesives and sealants is accomplished robotically in many industries. The following robotic dispensing applications of adhesive and sealant, are taken from the automotive industry where the majority of robotic dispensing applications are used.

#### Interior Seam Sealing

This application involves the sealing of body joints necessary for the unibody construction of automobiles. These seals are critical because they seal the passenger compartment from moisture, dust, and wind noise. Any one of

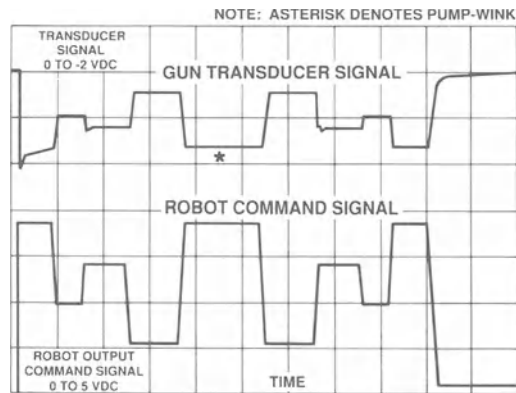


Fig. 8. Variable orifice gun response to input command signal from robot. (Courtesy Nordson Corporation, Amherst, Ohio.)

these quality defects resulting from improper seam sealing can lead to costly warranty repairs for the automotive manufacturer. For interior seam sealing the bead applied has a ribbonlike appearance that is generally 0.75–1.50 in. wide and 0.050–0.125 in. thick. In order to achieve this ribbonlike deposition, an air mix airless paint tip is used. The air mix, which uses various combinations of horn and face air, produces fan or conical spray patterns. The conical spray pattern is predominantly used because little or no orientation of the spray pattern is required relative to the substrate. The net result is more time to dispense with less time used to orient the robot wrist to achieve a directional spray pattern. Inadequate management of the bead as the robot varies its velocity results in nonuniform material deposition.

Figure 9 shows the typical seams to be sealed on an automotive chassis. This sealing process is normally found in an area in the plant known as the paint shop. The sealant material is applied immediately, prior to topcoat paint processes. The ensuing paint ovens then cure both the paint and sealant.

Typical equipment configuration for robotic seam sealing includes high response variable

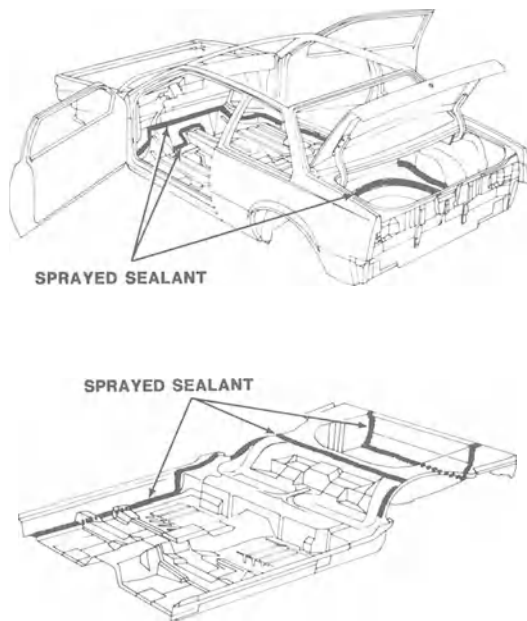


Fig. 9. Typical seams to be robotically sealed on an automobile chassis.

orifice guns, recirculating pumping systems and material temperature conditioning elements.

The materials applied for interior seam sealing are predominantly *plastisol sealants*. These plastisol materials may be complex rheological systems designed to promote interactions between the suspended component particles, yielding unique pumping characteristics. These interactions form a network which raises the material's inherent viscosity. However, when the material is sheared by pumps, fittings, hoses, and pipes, the network is broken down and the viscosity returns to a lower stabilized value. The material is said to be thixotropic when it displays this type of shear-thinning rheological behavior. Shear-thinning material behavior is desirable, as it allows the material to be sprayed without regard to orientation of the vehicle body without running, dripping, or sagging. Material recirculation throughout the dispense system prior to daily startup of production allows stabilization of material viscosity to ensure consistent spray patterns and ribbon depositions, critical to the success of the robotic installation.

Another material property that can influence spray pattern and ribbon deposition is temperature-induced viscosity variation. In general, as the material temperature is raised (usually due to changes in ambient air temperature), the material viscosity will also decrease. To minimize the impact of temperature changes on the material viscosity, the material can be temperature conditioned. There are two strategies for material temperature conditioning. The first technique is to water jacket the header system to provide heating and cooling for viscosity stabilization. Traditionally the temperature has been set at 70°F to stabilize material viscosity. The major drawbacks for this type of system are cost, reliability, and maintenance. Because of the water lines, heat exchangers, pumps, and installation complexity, the cost for such a system is often high. Reliability and maintenance of the system also play an important role, especially if the pumps or heat exchangers fail, allowing inconsistent material temperature. Since the material is no longer temperature conditioned, variations in spray pattern or ribbon deposition result.

The second method of temperature condi-

tioning uses heaters and sensors across the distribution path. This system temperature conditions the material by applying heat in the header system equivalent to the maximum ambient temperature. The system utilizes a modular piping network outfitted with zoned temperature controls (similar to Fig. 1) that allow the materials temperature to be gradually raised to the desired application temperature. The two basic pieces of information required to correctly apply this system is the temperature-viscosity curve for the material and the maximum recommended material application temperature. Since the material temperature is equal to ambient temperature while in the bulk drum, during storage and shipping, raising the material temperature so it is slightly below the maximum ambient temperature minimizes viscosity variations. Stabilized material viscosity provides uniform spray depositions on the automobile seam. Material temperature conditioning equipment of this type should include a header system with machine wound heater tape on the pipes for uniform heating and temperature control. A control system is required to accurately measure and control the temperature to  $\pm 1^\circ\text{F}$ . Maximum uptime is achieved with modular/zoned temperature controls. Should one of the zones deviate from the temperature set point, the controller can automatically turn that zone off while continuing to run the remainder of the system with adequate temperature conditioning. Fig. 10 shows a robotic spray sealer application gun reaching across the inside of a vehicle applying a ribbon of material to the automobile seams.

### Adhesive Bonding of Automotive Doors

As competition for automotive market share continues to intensify and manufacturers extend warranties for corrosion protection, adhesive bonding of components rather than spot welding has become the required assembly technique. Many of today's automobiles are constructed with two-sided galvanized sheet metal. When the galvanized metal is spot welded, the galvanization is burned through, leaving an area vulnerable to corrosion. In addition, spot welding in certain areas of the automobile is labor intensive and may require

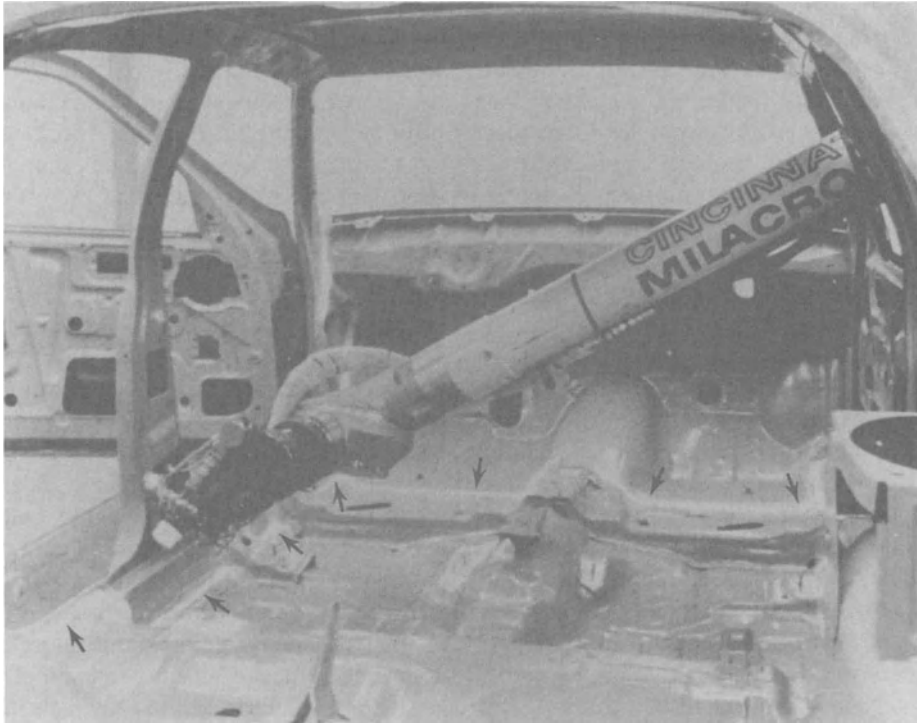


Fig. 10. Robotic seam sealing; arrows point to seam.

time to repair and touch up for customer acceptance.

This application covers adhesive bonding of the hem flange for automotive doors. For hem flange bonding the door is made up of an inner skin and an outer skin. The inner skin mounts the lock and window mechanisms as well as the various trim pieces, hinges and crash bar while the outer skin provides design contour and accepts the color coat of paint.

The process of building door assemblies requires the application of a structural adhesive to the outer door panel. The next step in the assembly of doors is the joining of the inner and outer panels. Finally, a hemming die is used to turn a small section of the outer panel over the inner panel to form a hem. Accurate bead placement and uniform material deposition are critical to achieve a structural bond. These requirements, combined with high production speeds, make hem flange bonding well suited for robotic automation. Fig. 11 depicts the entire door assembly line process complete with hemming die and induction cure fixture. The induction cure fixture applies localized

heating that causes the material to cure to a green strength sufficient to hold the door in position during shipping and handling until the final cure in the assembly plant paint ovens.

Figure 12 depicts the process of joining inner and outer panels. When the hem is formed by the dies, the bead of material is pressed out to form a thin film of adhesive between the two door panels. If too little material is applied, a film bond of inadequate strength is formed between the two panels. On the reverse side, if too much material is applied to the outer panel, excess adhesive will be forced out of the hemmed joint (known as squeeze-out) during the hemming operation, causing contamination of the die tooling. As this adhesive begins to build up on the die, it often transfers to the door assembly and results in expensive rework after final paint has been applied. The other drawback to squeeze out is in the area of increased maintenance for the hemming dies. Over time, the material builds up on the die and hardens, ultimately requiring a rework to maintain die specification.

The best solution to meet hem flange appli-



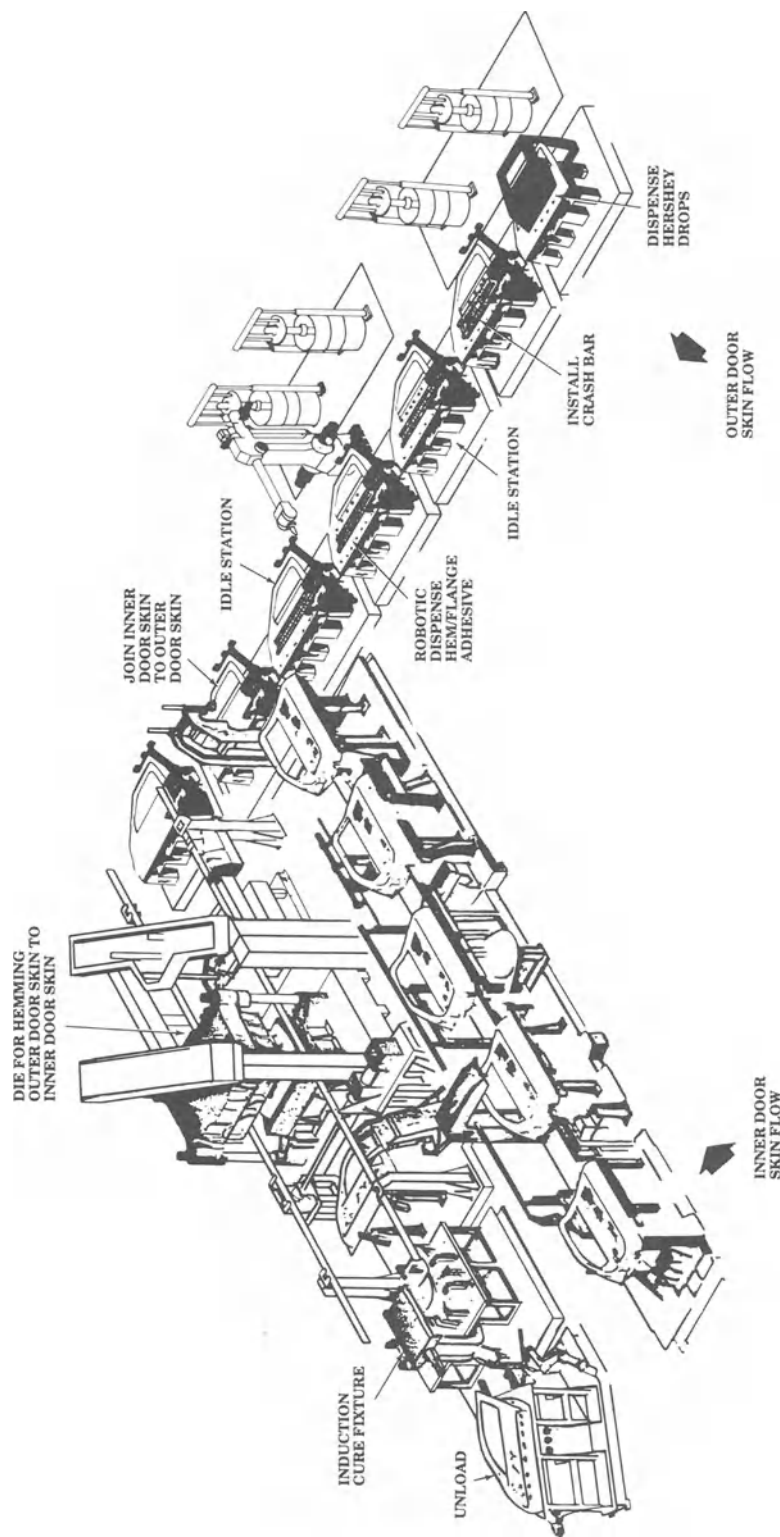


Fig. 11. Typical door assembly line at a stamping plant or in the body shop of a final assembly plant.

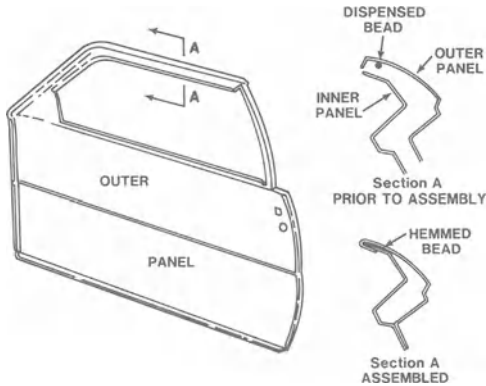


Fig. 12. Adhesive bonding of an automobile door hem flange.

cation requirements is to use a robot to position the dispensing gun around the programmed path and to utilize a dispensing system with sufficient response to adequately control the size of the bead regardless of velocity changes. It is not uncommon for doors to have a 0.120 in. bead that is 100 in. long robotically dispensed in 4 sec. Generally, two robots are used, with one robot applying adhesive around the window frame area while the second robot applies adhesive around the perimeter of the lower half of the door. Systems are often set up to ensure maximum production by having the two robots back each other up. Should one of the robots have a failure of some type, the second robot

would run in a mode known as *degrade* and execute both robot programs in an effort to maintain production. The upper robot velocity limit for dispensing material has traditionally been 30 in./sec, with 20 in./sec being the average velocity for dispensing material. Material temperature conditioning is also appropriate for hem flange bonding. For this application, the material is heated to about 82°F to stabilize the viscosity as well as to ensure that the material has enough heat to wet out the oily metal and provide good adhesion to avoid movement of the bead until it has been hemmed in the manufacturing process.

### Windshield Bonding and Body Shop Robotic Sealing

Figures 13 and 14 depict possible robot system configurations for windshield bonding and body shop sealing. All of the applications mentioned have similar considerations for evaluation of robotic applications. The common considerations for robotizing these and other adhesive and sealant applications include required bead profile (round, flat, or triangular); instantaneous flow or delivery rate; robot speed, accuracy and repeatability; and workspace of the robot.

Windshield bonding often requires the dispensing of a triangular bead at 10–18 in./sec.

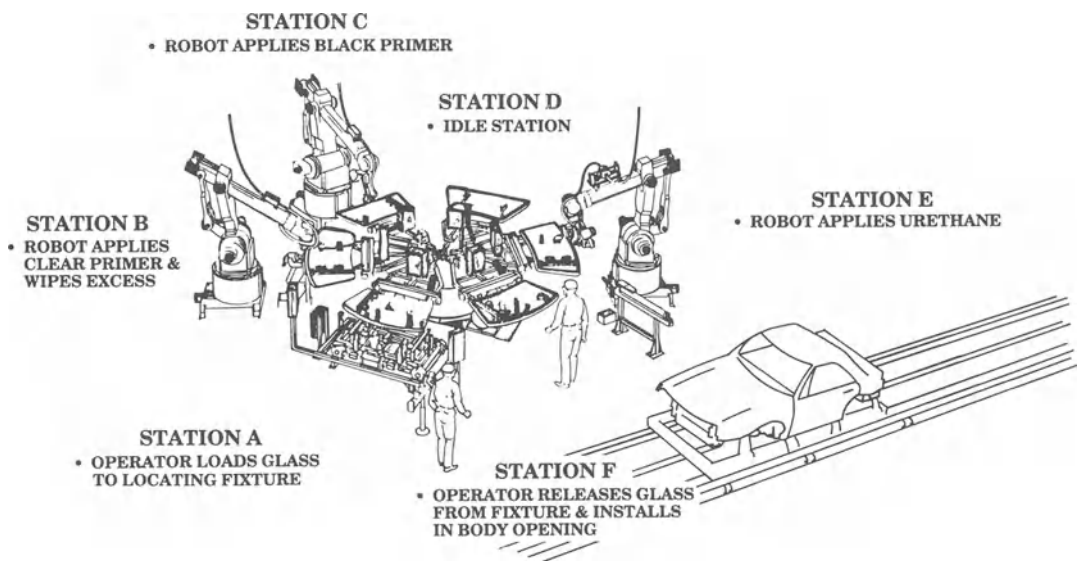


Fig. 13. Trimline windshield primer and urethane robotic application.

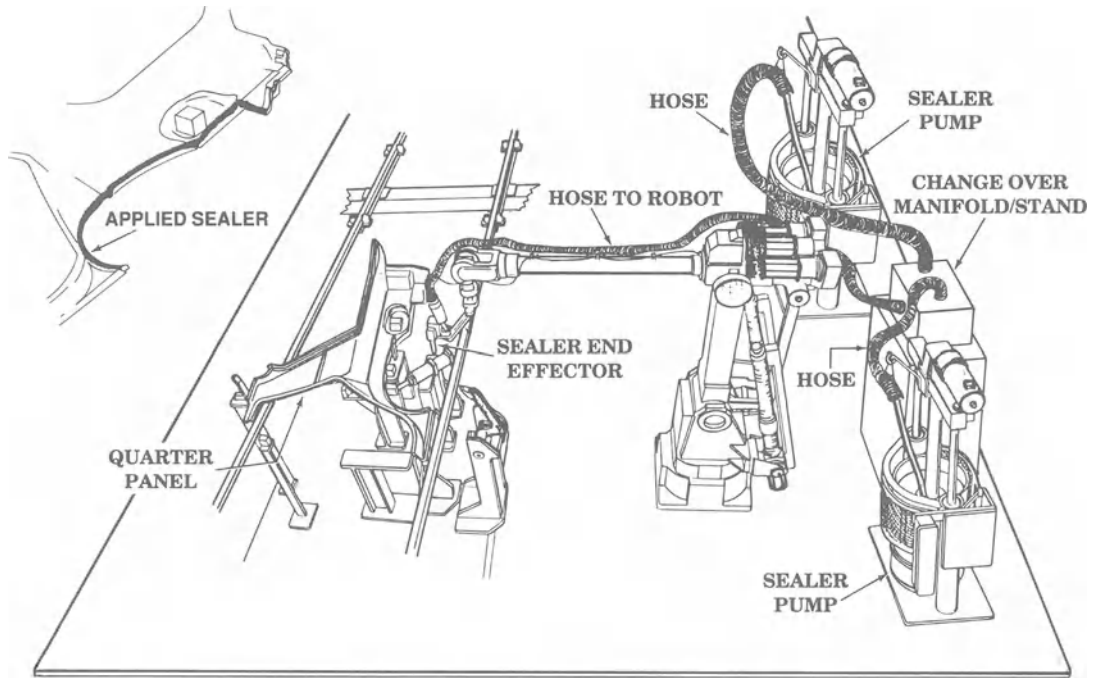


Fig. 14. Robotic sealing in the body shop.

The dispensing of a triangular bead that has a base dimension of 0.400 in. and a height of 0.470 in. requires that the gun nozzle be constantly oriented about the glass to obtain the desired bead profile.

The material traditionally used in windshield bonding has been a single-component moisture-cure *urethane*. These urethanes are often high in viscosity resulting in high application pressures to meet the robotic dispense rate.

Robotic sealing in the body shop, like seam sealing and door assembly, is performed to seal out dust and moisture while protecting weld locations from corrosion due to the galvanization being burned off. The bead dispensed is nominally a 0.160–0.200 in. diameter, at velocities that approach 20 in./second. The robotic systems used in this system are similar to Fig. 1.

The materials used in body shop sealing vary in application temperature. Traditionally, cold (or ambient) materials are applied during sheet metal body construction. In some instances, cold body shop sealers have caused manufacturing difficulties in ensuing production operations, for example, during the phosphate process. In those assembly areas where material washout has caused quality or process

problems affecting the paint finish or phosphate washer, the best solution has been to dispense a warm or hot applied weldable sealant. These materials are able to bite through the oils on the sheet metal to ensure good adhesion.

### DEVELOPING A ROBOTIC SYSTEM\*

When developing a robotic system for product assembly using adhesives, sealants, or gaskets, the following procedures may be useful:

#### Set Up a Team

- Establish a project team with representatives who have strong managerial, organizational, and technical skills. It is important to establish a competent team because the equipment includes sophisticated electronics, mechanics, application, and interface equipment.
- If a consultant is considered, choose one who has experience with robotics and is familiar with your manufacturing process.

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**Select Proper Tasks**

- Start simple. Do not become involved in something overly complex, particularly if this is your first experience with robots.
- To begin, identify tasks that will not require major changes in the manufacturing process.
- Define a task that which requires only one type of application equipment.
- Define material requirements for the task.
- If the application requires only one or two axes of movement, then some other form of automation may be better. However, batches of simple operations can be combined at some centralized location where robots can provide the flexibility to handle a variety of operations which would otherwise each require its own equipment design.
- Product variety for one robot is limited by its memory size. Check for both the number of positions and programs that the robot can store.
- Be sure that the part can be accurately positioned in the robots workspace. It is generally less expensive to design new fixtures than to modify existing fixtures.
- Construct a work flow chart.

**Define Objectives****Quality.**

- Define requirements for the accuracy, uniformity, and consistency of the bead of the hot melt (adhesive or sealant).
- Discuss the equipment quality record. Identify the expected time interval during which the system will operate reliably and the service requirements.
- Identify who will have responsibility for installation and service of the system.
- Identify which standards are applicable to the system.

**Productivity.**

- Establish cycle time goals for each application.
- Define the minimum amount and frequency of downtime for the system.
- Develop backup procedures.

**Cost Savings.**

- Calculate material and labor savings.
- Identify expenses for the equipment, manufacturing analysis, and relocation of equipment.
- Investigate tax credits.

**Safety.**

- Define systems and precautions that are necessary.

**Training.**

- Consider impact to workforce and what retraining will be involved.
- Identify who will need training and on which parts of the system.
- Determine how and where the training will be given.
- Recognize the benefits of the exposure to automation for other manufacturing operations.

**Future Requirements.**

- Discuss how needs and processes may change in the future and how the flexibility of the robotic system can contribute to those changes.

**Design the System**

- Involve materials, application equipment, and robot vendors early in the design process.
- Understand the interrelationship of each piece of equipment and identify one vendor who will coordinate these interrelationships.
- Ask for trials with your product and materials.
- Identify how part positioning and part identification requirements will be designed and controlled.
- Determine how much the present facility will have to be redesigned.

**ACKNOWLEDGMENT**

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